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THE

PHYSICAL REVIEW

THE GENERAL LAW OF FALL OF A SMALL SPHERICAL BODY THROUGH A GAS, AND ITS BEARING UPON THE NATURE OF MOLECULAR REFLECTION FROM SURFACES

By R. A. Millikan

Abstract

Law of fall of a small spherical body through a gas at any pressure.— (1) *Theoretical derivation.* When the ratio of free path to radius of droplet, l/a, is small, the resistance to motion is due entirely to viscosity and is proportional to a, while when l/a is large the resistance is due entirely to the inertia of the molecules hit and is proportional to a^2. The equation: $F=6\pi\eta av[1+A'l/a]^{-1}$ satisfies both these theoretical conditions. From Kinetic theory, however, it has been shown that A' is not constant but varies from a lower theoretical limit of .7004 (diffuse reflection) for l/a small, to 1.164 for l/a large. We therefore put $A'=A+B\epsilon^{-ca/l}$ and write the complete equation: $F=6\pi\eta av[1+(A+B\epsilon^{-ca/l})l/a]^{-1}$. (2) *Experimental verification.* By the oil drop method, values of A' have been determined for a wide range of values of l/a, from 0.5 to 134, for oil drops in air. These results are found to agree within the experimental error of ± 2 per cent or less with the theoretical equation, and give $A=.864$, $B=0.290$, $c=1.25$. A discussion of results obtained with other drops indicates that while A varies with the nature of the gas and even more with the material of the droplet, $(A+B)$ is within two or three per cent the same for most sorts of particles which might settle through the atmosphere. (3) *Differentiation between diffuse reflection, specular reflection, radial reflection, and condensation and re-evaporation of molecules.* Radial reflection is shown to be thermodynamically and dynamically impossible; condensation and re-evaporation to be inconsistent with the observed value of (A+B). This observed value is satisfied only by a combination of about 1/10 of specular reflection with 9/10 of diffuse reflection, this last being defined as a re-emission from each element of surface and in such directions as to satisfy the Maxwell distribution law, of all molecules which impinge upon that element. The agreement adds new evidence for the existence of specular reflection of molecules since 1/10 had also been indicated by the values of A previously obtained for oil-drops in air. (4) *Effects of mechanical roughness of the surface.* The apparent discrepancies between the author's results and those of Knudsen and Gaede, which seemed to indicate complete diffuse reflection, are explained by the effects of minute mechanical protuberances which are thought to have existed on the insides of these authors' capillary tubes.

1. Introduction

IT is well known that Stokes' law of motion of a sphere through a homogenous medium which does not slip at all at the surface of the sphere, namely,

$$F = 6\pi\eta a v \tag{1}$$

is obtained by neglecting entirely the resistance which arises from the inertia of the medium, the "push resistance," and considering the force opposing the motion to be due solely to shear, the "drag resistance," and therefore to arise wholly from the viscosity of the medium.[1] It is also well known that this assumption is valid provided the velocity is small compared with $\eta/\rho a$,[1] or, referring to Arnold's accurate experiments,[2] provided a is less than 6/10 of the so-called critical radius $\bar{a}$ defined by $\bar{a} = \eta/\rho v$.

Stokes' law is then applicable to spheres falling under gravity, first, when they are so small that the foregoing condition is fulfilled, and, second, when the medium may still be regarded as homogeneous and therefore as non-slipping.

In liquids this last condition may be considered as fulfilled for spheres of radii greater than 10^{-6} cm, so that Stokes' law of fall is presumably rigidly applicable in liquids to spheres of radii between the wide limits 10^{-2} and 10^{-6} cm.[3] In gases at ordinary pressures, however, it has been shown[4] that the slip due to the molecular inhomogeneities causes the law to be slightly incorrect even for spheres of radii as large as 0.005 mm, and that Eq. (1) must then be replaced by an equation of the form

$$F = 6\pi\eta\, a\, v/(1 + Al/a) \tag{2}$$

in which A for different gases and different drop-substances was found to vary between the limits 0.7 and 1.0, and in which the lower theoretical limit for A was found from simple hydrodynamical considerations to be 0.7004[5] when l is defined by $\eta = .3502\rho\,\bar{c}l$.

Since the denominator in (2) is merely a small correction term to Stokes' law and has been developed by introducing into the hydrodynamical considerations underlying that law the single additional assumption of surface-slip due to molecular inhomogeneities, it is clear

[1] C. G. Stokes, Cambr. Trans. 9, 1851, and Mathematical and Physical Papers, **3**, 59. See also Lamb's Hydrodynamics

[2] Arnold, Phil. Mag. **22**, 755, 1911

[3] Arne Westgren, Zeit. Phys. Chemie **89**, 63, 1914

[4] Millikan, Phys. Rev. **32**, 376, 1911

[5] Millikan, Phys. Rev. **21**, 217, March, 1923

that the *assumption of a resistance due to viscosity alone is inherent in the validity of Eq.* (2) as developed in the articles referred to. It should be noted, also, that the derivation of (2) is only valid for values of Al/a which are small in comparison with unity.

But it is extremely interesting to know the *complete* law of motion of small bodies coming to the earth from great distances through very rarified atmospheres and reaching Stokes' law merely as a limit in the dense atmosphere near the earth's surface. The accurate experimental determination of this law is the first result of the present investigation. A second result is the interpretation of this law from the point of view of the theory of molecular reflection from liquid and solid surfaces.

It was in 1909 and 1910 that the first experiments[6] were performed which showed that the simple law of fall given in (1) had to be changed to the form given in (2) in order to account for observed rates of fall, and in these first experiments the value of A was given as .817. In 1911 McKeehan[7] verified these results by an independent, though perhaps somewhat less precise method, and wrote the law of fall of wax spheres through air in the same form, but with A having the value 1.00 instead of .817. During the same year, however, my own observations showed that it was impossible to represent the *complete* law of fall by an equation of the form of (2), and in 1912 the first direct determination of this complete law was published[8] very briefly and without comment in the form

$$F=6\pi\eta\, av/[1+l/a\ (A+B\epsilon^{-c\,a/l})] \tag{3}$$

The constant A was here given as .874, B as .35, and c as 1.7. Further, in 1911 Knudsen and Weber[9] had arrived by an *indirect* method, namely by observations on the damping in a vessel at very low pressures, of two glass spheres tortionally suspended in a horizontal plane at the ends of a thin rod, at a resistance equation of the same form but with different constants, which they wrote as follows:

$$F=6\pi\eta\, a\, v/[1+.68\, l/a+.35 l/a\ \epsilon^{-1.85a/l}] \tag{4}$$

These purely empirical equations of Knudsen's and the author's, the likenesses and differences in which will be considered later, have up to the present time been given no theoretical interpretation whatever, but the reasoning which lead the author, at least, to adopt this particular form of empirical equation is as follows.

[6] Millikan, Science, **32**, 436–443, 1910, and Phys. Zeit. **11**, 1097–1109, 1910; Phys. Rev. **32**, 351–397, 1911

[7] McKeehan, Phys. Rev. **32**, 341, 1911

[8] Millikan, British Association Reports, Dundee, 1912, p. 410

[9] Knudsen and Weber, Ann. der Phys. **36**, 982, 1911

2. Theory

As indicated in the foregoing, the sole appreciable cause of resistance to the motion of a small sphere through a dense gas is the *viscosity* of the medium. In a very highly rarefied atmosphere, however, it is evident that this cause drops out entirely, and the sole appreciable cause of resistance is then the inertia of the molecules which are being *directly* encountered per second by the sphere. When, with decreasing pressure, this latter condition has been fully reached the resistance must be proportional to the number of molecules encountered per second, that is to the cross section of the sphere or to the square of the radius; whereas at the other extreme, i.e., at high pressures where viscosity is the sole appreciable element, the resistance is proportional, as indicated in (1), to the first power of the radius.

It will be seen at once that both of the foregoing conditions are realized by giving the correction term to Stokes' law, as was done in (2), the form $(1+Al/a)^{-1}$; for so long as $A\,l/a$ is small in comparison with unity, the denominator of (2) remains essentially unity and F is then proportional to a, but when l/a is so large that 1 is negligible in comparison with $A\,l/a$, F becomes proportional to a^2. In other words, *so far as form alone is concerned, (2) is adapted to express the necessary relations between F and a, both at high pressures where viscosity is the only essential factor in the resistance, and also at very low pressures where viscosity plays no appreciable role in the resistance.*

But there is no reason whatever for supposing that the necessary linear relation between F and a^2 at low pressures, and the equally necessary linear relation between F and a at high pressures correspond to the same value of the constant A, for this constant appears for wholly different reasons in the two cases. It has been shown, as indicated above, that for sufficiently high pressures, that is for small values of l/a, the lowest possible value of A, that corresponding to diffuse reflection or to condensation and evaporation, is 0.7004. At the other extreme, when l/a is very large in comparison with 1, it may also be shown theoretically (see below) that the lowest possible value of A is larger than 1. But throughout each of these two regions, first, that in which Stokes' law is just beginning to break down, and, second, that in which the gas is very rare, A must be a constant.

Now it has also been shown[10] that so long as A is a constant its value in an equation of the form of (2) may be easily and accurately determined experimentally by observing the slope of the necessary linear relation

[10] Millikan, Phys. Rev. **32**, 378, 1911

between $e_1^{2/3}$ and l/a in the characteristic equation of the oil-drop method, namely $e_1^{2/3}=(1+A\ l/a)e^{2/3}$. Any generalized law of fall, then, which will connect the two resistances, the one close to where Stokes' law is valid, and the other corresponding to very low pressures where Stokes' law fails entirely and F is proportional to a^2, must contain a term of such form as to make the linear relation between $e_1^{2/3}$ and l/a corresponding to a *small* value of A (e.g., .700) pass over into another linear relation between $e_1^{2/3}$ and l/a corresponding to a larger value of A. Since, then, for the purposes of this complete law of fall, A must be considered a variable, I propose henceforth to call this variable A'. The form, then, which must be given to A' to make it execute such a shift as that just described from a low constant value to a higher constant value is clearly as follows

$$A'=A+B\epsilon^{-c\,a/l} \tag{5}$$

for when l/a is small the second member reduces to zero and A' to A, while when l/a is large the exponential term becomes unity and A' changes to $(A+B)$. The constant c may be given a value to correspond to any rapidity of shift.

In the oil-drop method of determining the complete law of fall then, the exponential term is merely a convenient device for causing one linear relation between $e_1^{2/3}$ and l/a to shift over into a second linear relation of larger slope, the cause of that shift being a transfer from a viscous resistance which is proportional to a, to a direct impact resistance which is proportional to a^2.

3. The Experimental Determination of the Constants $(A+B)$ and c

Because of the very great significance, to be presently pointed out, of the constants A and $(A+B)$ for the theory of reflection of molecules, a great deal of attention has been devoted to their accurate evaluation for different gases and different surfaces. So far as A alone is concerned, this work has already been fully reported.[5] The work from which had been derived the values of A, B, and c, published in 1912, had been carried carried only up to a value of $l/a=12$, which was insufficient to determine these constants with accuracy. Since then, however, I have taken very long series of elaborate observations by the oil-drop method for the sake of determining A, B, and c with much greater precision.[11] In this work oil drops have been observed at pressures ranging from 760 mm down to 1.6 mm, and at values of l/a from .1 to 134, i.e., over a range of

[11] See Phys. Rev. **15**, 545, 1920, for first publication of corrected form of complete law of fall.

TABLE I

Observations on Three Drops

t	t_F	n'	$\frac{1}{n'}\left(\frac{1}{t_{F'}}-\frac{1}{t_F}\right)$	n	$\frac{1}{n}\left(\frac{1}{t_g}+\frac{1}{t_F}\right)$
(1)	(2)	(3)	(4)	(5)	(6)
Drop No. 10					
37.77	29.58			7	.008765
37.90	29.06				
37.96	39.06			6	.008676
		2	.008652		
37.69	120.50			4	.008682
38.03	121.41				
		2	.008546		
37.82	39.48			6	.008625
38.09	39.58				
		1	.008831		
37.77	60.85			5	.008575
		1	.008361		
38.37	40.33				
37.35	40.72			6	.008520
37.67	40.56				
		1	.008801		
37.68	63.08			5	.008462
37.35					
Mean 37.80			.008636		.008615
Drop No. 23					
50.42	64.34				
51.01	64.80			1	.035264[2]
49.77	66.79				
50.27	65.28				
50.33		1	.033159	2	.034212[1]
49.42	20.46				
49.67	20.79				
Mean 50.13					.034913
Drop No. 47					
8.9	12.4				
8.7	12.5				
10.0	12.5				
9.0	12.9			8	.02316
9.3	13.4				
9.9	13.0				
10.2	13.2				
9.9	12.8				
		1	.02263		
9.2	18.2				
9.2	18.0				
9.0	17.7			7	.02347
9.4	17.7				
9.0	17.5				
9.3	16.5				
9.0	17.4				
		1	.02453		
9.0	28.7				
9.1	29.4			6	.02363
	26.7				
Mean 9.31			.02358		.02346

values varying 1300 fold. Out of 50 oil drops whose values of l/a are scattered somewhat uniformly over this whole region, three have been selected for presentation in Tables I and II. These are merely typical drops which will indicate to the reader the kind of precision obtained. As shown in Table II, for the three drops selected, the pressures were 5.33, 2.33, and 0.237 cm and the values of l/a, 1.2806, 6.459 and 105.08. The pressures were observed accurately with a very sensitive McLeod

TABLE II

	Drop No. 10	Drop No. 23	Drop No. 47	Units
Vi	1336.1	670.3	20.3	volts
Vf	1336.1	668.8	20.3	volts
t	22.98	22.99	21.8	°C
p	5.33	2.329	0.2372	cm Hg
v_1	.02704	.02039	.10966	cm/sec
a	10.50	4.77	2.905	10^{-5}cm
$1/pa$	1789.3	9024.8	14,683	
l/a	1.2806	6.459	105.08	
$e_1^{2/3}$, observed	136.88	501.6	7383	10^{-8}
calculated	137.3	496.6	7449	10^{-8}
A', observed	.968	1.118	1.151	
calculated	.973	1.103	1.144	

gauge. The notation used in recording these drops is the same as that which has been generally adopted; i.e., the column headed t_g represents the time in seconds which the drop required to fall the distance between cross-hairs, a distance which varies somewhat in some of these experiments, but was generally about a centimeter, its accurate value being always obtainable from the value of the velocity v_1 (Table II) and the value of the time t_g. The second column gives the time required for the drop to rise against gravity between the same cross-hairs when the voltage given in Table II under the heading V_i and V_f (initial and final) was applied between the plates. The third column gives the number of electrons by which the charge on the drop was changed when the value of t_F changed as indicated in the second column. The fourth column gives the value of the electronic charge in terms of a velocity as computed from each individual change in charge. The fifth column gives the total number of free electrons in the charge of the drop corresponding to various values of t_F. The sixth column gives the value of the electronic charge in terms of a velocity as computed from t_g and t_F.

The accuracy of the work can be gauged from the sort of agreements found in columns 4 and 6, also from the differences in Table II between the observed and the computed value of $e_1^{2/3}$ and A'. As Table I shows, at these very low pressures the velocities are so high and the fluctuations due to Brownian movements have so largely increased that the errors are

perhaps ten times as great as at ordinary pressures. This means that the values of $e_1^{2/3}$ and A' for the individual drops may be as much as 1 or 2 per cent in error.

Tables III and IV give the complete tabulated results obtained on all the drops. Especial attention may be directed to the last column of

TABLE III

Drop No.	$t°C$	$P.D.$ (volts)	V_1 (cm/sec.)	(V_1+V_2) (cm/sec.)	n	a (10^{-5}cm)	p (cm Hg)
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
*1	23.05	2006	.05786	.004545	15–20	19.19	7.60
2	23.00	1684	.1123	.002652	44–86	26.59	5.29
*3	23.04	2005	.04170	.005836	9–18	15.82	7.72
4	22.83	2556	.03193	.008250	4–7	13.76	8.82
5	22.87	1711	.03403	.005802	4–10	13.83	7.55
*6	23.04	2001	.03348	.008116	5– 7	12.41	7.95
7	23.04	1688	.07345	.004057	20–28	20.05	4.90
8	23.05	1684	.05989	.005010	8–12	14.24	5.70
9	23.07	1681	.04098	.006216	7–12	12.85	5.96
*10	22.98	1336	.02704	.008615	4– 7	10.50	5.33
11	23.06	1684	.02334	.012000	5– 7	9.52	5.44
*12	23.10	1321	.04353	.011601	4– 7	11.14	2.97
13	22.8	861	.02866	.009287	5– 8	8.88	3.65
14	23.15	672.6	.06708	.005040	13–15	13.84	2.18
15	20.3	842	.01981	.01989	1– 4	6.05	3.23
16	23.23	850.5	.01985	.02220	1– 4	5.85	3.11
17	21.0	843.0	.02854	.01899	2– 4	6.89	2.57
*18	22.98	671	.03089	.01834	2– 4	6.79	2.22
19	21.2	167.7	.03523	.005256	8–11	6.60	1.91
*20	23.06	673.6	.01504	.034278	1– 3	4.34	2.86
*21	23.10	674.3	.01421	.040623	1– 3	4.03	2.81
22	21.5	339.0	.03890	.011843	5– 9	6.61	1.73
*23	22.99	669.5	.02039	.034913	1– 2	4.77	2.33
*24	23.00	673.5	.01679	.04104	1– 3	4.24	2.48
25	20.25	343.0	.04093	.01308	4– 7	6.53	1.58
*26	23.80	169.0	.01651	.01225	2– 4	3.99	2.31
27	19.7	336.0	.05844	.01908	5– 7	6.43	1.11
28	21.4	508.5	.02717	.05018	1– 2	4.14	1.51
29	22.47	70.1	.06474	.01922	5– 7	2.640	.962
30	21.2	103.4	.11386	.01133	10–15	6.431	.5332
31	21.5	36.4	.06609	.01766	6–10	2.588	.790
32	21.2	68.9	.10527	.01272	11–13	5.281	.4656
33	21.8	14.1	.10558	.00832	17–22	3.588	.536
34	21.3	75.5	.08046	.02890	4– 5	3.787	.435
35	21.3	80.7	.05617	.04315	2– 4	2.711	.4925
36	21.5	116.7	.05174	.06920	1– 3	2.825	.4933
37	21.3	100.3	.06912	.05412	2– 3	3.213	.4220
38	21.5	143.1	.11421	.06648	2– 4	3.991	.3223
39	21.4	69.5	.14503	.03208	5– 8	4.329	.2755
(1) 40	23.4		.09903		3–10	3.447	.3192

*Starred drops were taken in a condenser of plate distance 1.49174 cm.
Unstarred drops were taken in a condenser of plate distance 1.598 cm.
(1) The voltage here had four values, viz. 24.0, 36.2, 51.2, 81.8.
The corresponding (V_1+V_2) were .014976, .022614, .031922, .04984.

TABLE III (continued)

Drop No.	$t°C$	P. D. (volts)	V_1 (cm/sec.)	(V_1+V_2) (cm/sec.)	n	a (10^{-5}cm)	p (cm Hg)
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
41	21.6	63.3	.11282	.04511	3– 4	3.454	.2782
42	22.6	49.8	.14565	.03258	6– 7	3.860	.2389
(2) 43	22.87		.15026		2– 3	3.869	.2320
(3) 44	19.8		.12492		1– 8	3.272	.2410
45	23.0	23.1	.14121	.01981	9–11	3.491	.2258
46	21.9	19.6	.19562	.01550	15–18	3.996	.1823
47	21.8	20.3	.10966	.02346	6– 8	2.905	.2372
(4) 48	22.2		.11013		2– 3	2.748	.2275
49	22.4	30.8	.09669	.05207	1– 3	2.452	.2318
50	23.0	19.4	.18633	.02385	7– 8	3.285	.1626

(2) The voltage here had two values, viz. 111.2 and 143.3.
The corresponding (V_1+V_2) were .07446 and .09581.
(3) The voltage here had four values, viz. 20.15, 38.5, 79.6, 155.2.
The corresponding (V_1+V_2) were .018619, .03567, .07229, and .14397.
(4) The voltage here had two values, viz. 43.3 and 66.3.
The corresponding (V_1+V_2) were .06038 and .09073.

Table III, which shows the total range of pressures used. It will be seen that these pressures are all below 9 cm, observations at higher pressures having been sufficiently reported in preceding papers,[12] and extend down to .16 cm.

In Table IV it will be interesting to observe that whereas in the tables and graphs previously published the values of $1/pa$ have been reported only as high as 480,[13] the values here begin at 686.7 and extend up to the huge value of 187,240, while the corresponding values of l/a run from 0.495 by fifty fairly uniformly distributed steps up to 134. Columns 3, 4, 5, and 6 show the agreement obtained between the observed values of A' and of $e_1^{2/3}$ and those computed from the final empirical formulas shown at the top of Tables IV. It will be seen from the last column that in general the error is but a fraction of a per cent, and in no case is it as high as 2 per cent.

A glance at the value of A' for the last thirteen drops of Table IV shows that the final value of $(A+B)$ has been reached within the limit of observational error for all these drops. Comparison of the second and fourth columns in the case of these drops shows that though l/a varied from 55 up to 134, A' does not change in that whole range by as much as one third per cent.

Figs. 1, 2, 3, 4, and 5 have been inserted for the sake of showing graphically the relations brought out numerically in Tables III and IV. Fig. 1 is a repetition of the previously published linear relations of $e^{2/3}$ and $1/pa$ up to values of the latter of about 500, which correspond to

[12] See, for example, Millikan, Phil. Mag. 34, 11, 1917
[13] See Phil. Mag. 34, 12, 1917

TABLE IV

$e_1^{3/5} = e^{3/5}(1 + A'l/a)$; $A' = .864 + .29\epsilon^{-1.25\, a/l}$

$1/pa$	l/a	A'(obs.)	A' (calc.)	e_1 (obs.) (10^{-9})	e_1 (calc.) (10^{-9})	Difference (per cent)
(1)	(2)	(3)	(4)	(5)	(6)	(7)
686.7	.4915	.887	.887	87.75	87.77	+ .02
711.6	.5093	.877	.888	88.42	88.78	+ .4
819.7	.5867	.888	.898	92.97	93.31	+ .4
823.2	.5892	.903	.898	93.80	93.46	− .4
957.8	.6855	.904	.911	99.00	99.29	+ .3
1014.8	.7263	.912	.917	101.6	101.9	+ .3
1018	.7289	.916	.917	101.9	102.0	+ .1
1223.	.8752	.946	.934	111.7	111.1	− .5
1301.	.9310	.940	.940	114.4	114.6	+ .2
1789.3	1.281	.968	.973	139.6	137.3	+ .3
1931	1.381	.975	.986	143.4	143.9	+ .4
3021.6	2.163	1.028	1.027	197.0	196.9	− .05
3083	2.207	1.048	1.029	202.4	199.9	−1.3
3511	2.513	1.027	1.041	218.9	221.0	+1.0
5070	3.620	1.078	1.070	299.7	297.9	− .6
5488	3.933	1.090	1.076	323.1	319.8	−1.0
5713	4.089	1.087	1.087	332.8	329.7	− .9
6644	4.756	1.078	1.088	374.4	377.4	− .8
8033	5.749	1.093	1.098	445.0	447.0	+ .4
8069.2	5.775	1.090	1.098	446.0	448.7	+ .6
8899	6.333	1.107	1.102	489.5	488.6	− .2
8905	6.373	1.111	1.103	494.0	490.8	− .8
9024.8	6.459	1.116	1.103	501.6	496.6	−1.0
9542.9	6.831	1.103	1.106	521.5	522.9	+ .3
9882	7.073	1.084	1.107	529.8	539.7	+1.9
10905	7.805	1.096	1.111	583.8	591.1	+1.2
14397	10.30	1.139	1.121	779.6	766.9	−1.6
16307	11.67	1.144	1.125	877.0	863.2	−1.6
26400	18.89	1.126	1.135	1361	1372	+ .9
29160	20.87	1.137	1.137	1511	1512	+ .007
38640	27.65	1.149	1.141	2002	1990	− .6
40670	29.11	1.142	1.142	2092	2093	+ .005
51940	37.17	1.145	1.144	2663	2660	− .01
60700	43.44	1.150	1.146	3113	3104	− .3
67590	48.37	1.147	1.147	3452	3452	0
71770	51.36	1.126	1.147	3597	3665	+1.9
73710	52.76	1.135	1.147	3721	3763	+1.1
78050	55.86	1.148	1.148	3980	3981	+ .03
83850	60.01	1.153	1.148	4289	4275	− .3
90826	65.00	1.152	1.149	4639	4626	− .3
104100	74.48	1.138	1.149	5243	5294	+1.0
108520	77.76	1.133	1.149	5439	5524	+1.5
111400	79.72	1.133	1.149	5583	5667	+1.5
126733	90.72	1.151	1.150	6443	6435	− .1
126900	90.82	1.152	1.150	6454	6445	− .1
141400	101.20	1.152	1.150	7190	7187	− .05
146830	105.08	1.144	1.151	7383	7449	+ .9
159900	114.45	1.161	1.151	8183	8114	− .9
175800	125.78	1.152	1.151	8926	8910	− .2
187240	134.00	1.167	1.151	9618	9488	−1.2

values of l/a of from 0 to .4. Fig. 2, which is a continuation on the same scale as Fig. 1 shows nicely how at about a value of $1/pa = 700$, or $l/a = .5$, this linear relation begins to break down, the last drop on Fig. 2 showing

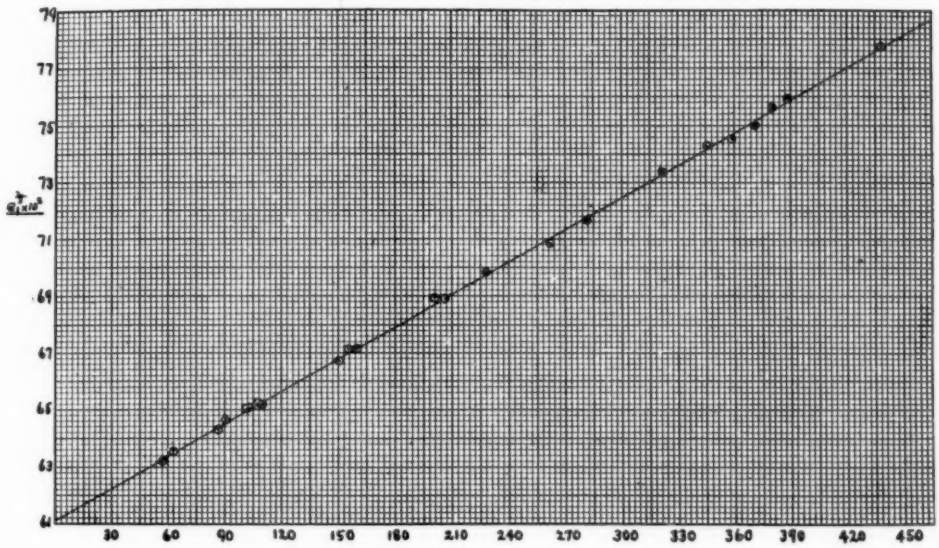

Fig. 1. $e_1^{3/5}$ as function of $1/pa$, for l/a up to 0.4.

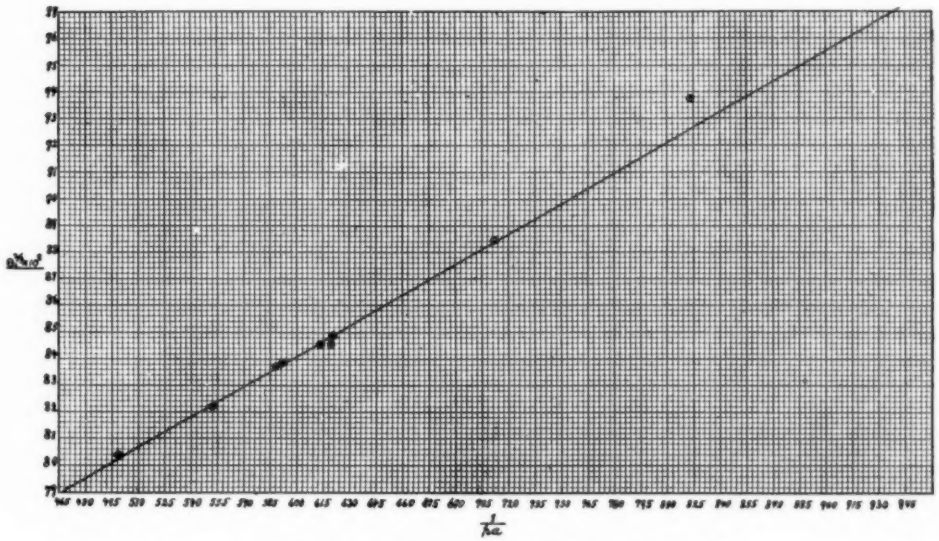

Fig. 2. $e_1^{3/5}$ as function of $1/pa$, for l/a 0.4 to 0.7.

a departure from the straight line much greater than the observational error. Fig. 3, which is on the same scale as the other two figures but con-

tinuing to the higher values of $1/pa$ shows this departure very strikingly. In Fig. 4 the $1/pa$ scale has been reduced to 1/20 its former value, and the progression of $e_1^{2/3}$ with $1/pa$ up to values of the latter of 7000 is shown. In Fig. 5 is shown on a scale about 1/400 of that used in Fig. 1, 2, and 3,

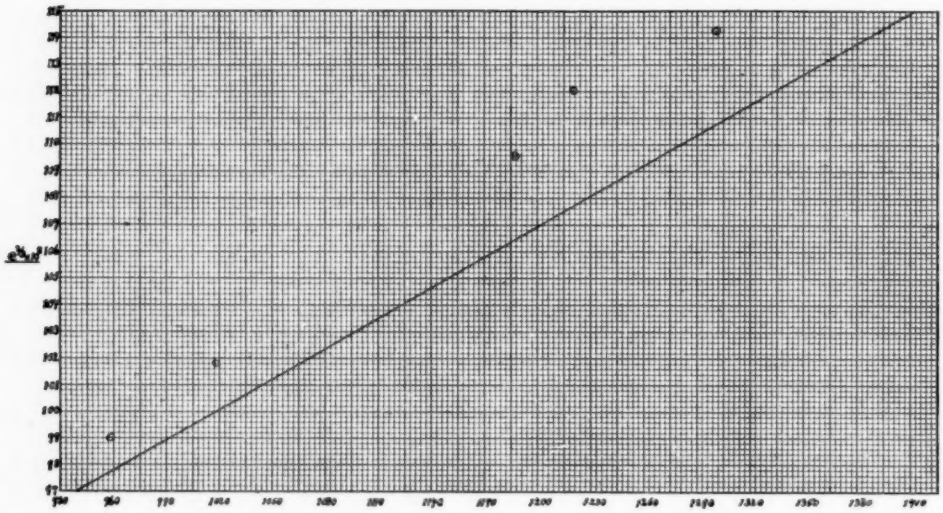

Fig. 3. $e_1^{3/5}$ as function of $1/pa$, for l/a 0.7 to 1.0.

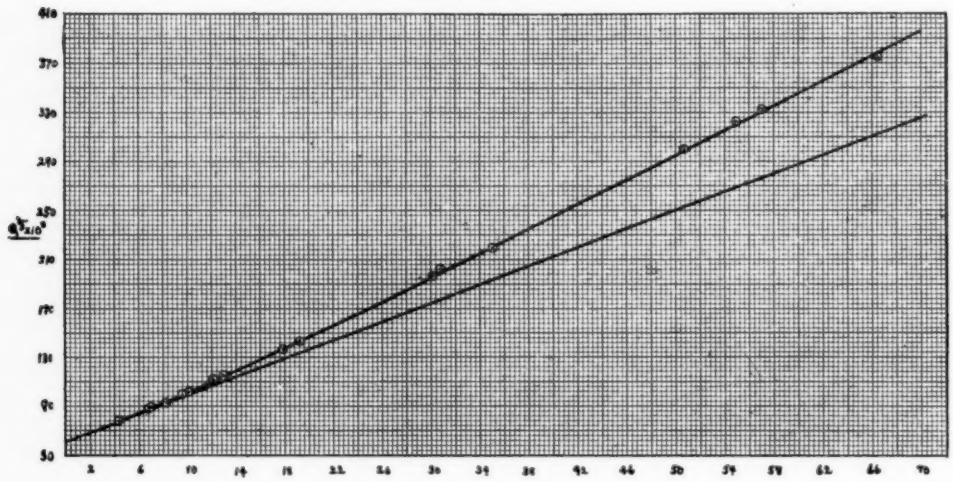

Fig. 4. $e_1^{3/5}$ as function of $1/pa \times 10^{-2}$, for l/a from 0 to 5.

the last twenty-eight drops at the end of Table IV. The first eleven drops on the left side of this scale may well be ignored, since, in view of the smallness of the scale, the error in plotting in this region is so large

as to nearly mask the fact that the drops are all slightly above the line as they should be. The last seventeen drops at the upper end of the scale brings out strikingly, however, how completely the final value of the slope has been attained. This makes it altogether unnecessary to push observations to any higher values of $1/pa$ since, from theoretical considerations previously advanced, it is necessary that this slope remain constant for all higher values. *It is clear, then, that we have obtained the general formula for the complete law of fall of a spherical liquid drop through air.*

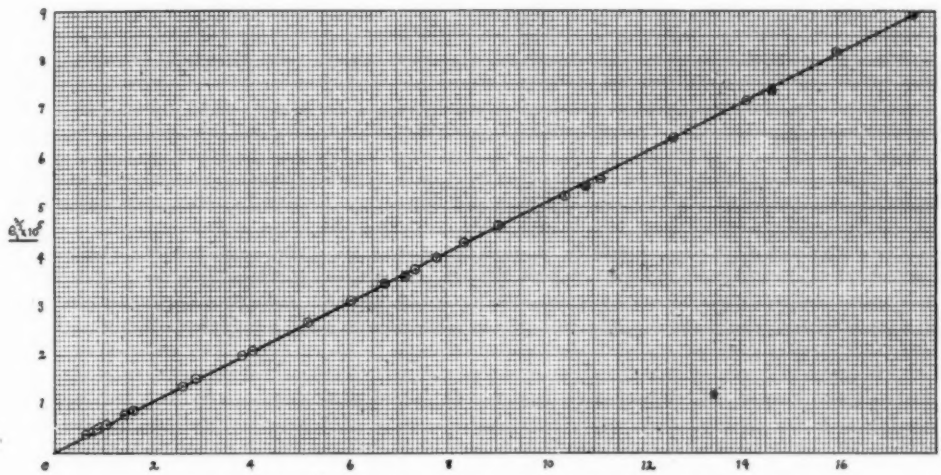

Fig. 5. $e_1^{3/2}$ as function of $1/pa \times 10^{-4}$, for l/a from 0 to 125.

4. The Significance of the Value of $(A+B)$

a. Possible modes of reflection of molecules. So long as the viscosity of the medium is the sole cause of the resistance, it will be seen from the method used[5] in deducing the lower limit to the theoretical value of A (.7004), that the tangential force on unit surface, which is what determines the value of A, is precisely the same whether the molecules are diffusely reflected from the surface, are condensed and reëvaporated without preference as to direction, or whether they are returned with a preference for the direction of the normal to the surface. For if the molecules coming out all emerge *symmetrically* with respect to the normal to the surface, they give up to it their total mean *tangential* momentum, and so exert the same drag quite independently of how they emerge, *provided, only, they have upon emergence no average component parallel to the surface.*

Not so at the other extreme where the gas is so rare that the resistance is to no extent a result of viscosity but is due wholly to the inertia of

those particular molecules which make direct encounters with the sphere, no streaming motion of the gas outside the cylindrical volume of section πa^2 having to be taken into account. If the character of these encounters be known, the resistance may be computed. But in this computation it is necessary to differentiate the four following cases:

Case A. Specular reflection. This case has been worked out by Langevin,[14] Cunningham,[15] Lenard,[16] and Epstein,[17] all of whom agree in finding the resisting force F acting on a sphere of radius a moving with velocity v through a gas of density ρ and average molecular velocity, $\bar{c}$ to be given by

$$F = (4/3)\pi\rho a^2 \bar{c} v \tag{6}$$

This case has, of course, no actual existence, but it is of importance to have it worked out because of the evidence recently brought forward[5] for the existence, quite in accord with the theory advanced by Maxwell[18] fifty years ago, of a definite fraction f of the molecules which are specularly reflected.

Case B. Condensation and re-vaporation. In this case all of the molecules are assumed to impinge inelastically and the emerging ones are assumed to come out in equal numbers from all unit areas of the sphere, and hence to exert no resultant force whatever upon it. This case has been worked out by Lenard[16] and Epstein,[17] who agree in finding the resistance precisely the same as in case A. Cunningham also gave a solution for this case, but appears to have made two numerical errors, one of which was pointed out in 1911,[19] and the other of which Epstein discusses in a following paper. When these errors are corrected Cunningham is brought into agreement with Lenard and Epstein.

Case C. Diffuse reflection. This case will be divided into two subcases. *In Case C_a, diffuse reflection, Lenard,* all of the molecules striking each particular element of the surface are assumed to emerge from that same element, each with its incident speed but in directions which are uniformly distributed over the hemisphere which faces the element. Both Lenard and Epstein have solved this case, and they agree in finding

$$F = (16/9)\pi\rho a^2 \bar{c} v.$$

Epstein's analysis shows, however, that this case cannot actually exist since it involves the same sort of a violation of the second law of thermo-

[14] Langevin, Ann. de Chem. et Phys. **5**, 266, 1905
[15] Cunningham, Proc. Roy. Soc. **83**, 359, 1910
[16] Lenard, Ann. der Phys. **61**, 672, 1920
[17] Epstein, Phys. Rev., August, 1923
[18] Maxwell, Scientific Papers, **2**, 705
[19] Millikan, Phys. Rev. **32**, 380, 1911

dynamics as will presently be discussed in connection with case D. It is here mentioned solely because of its historical interest.

In Case C_b, diffuse reflection, Epstein, which will be understood henceforth when the term "diffuse reflection" is used without qualification, the assumption is the same as in C_a in that all of the molecules incident upon a given element of surface must emerge from that same element, but it differs in that the distribution of the emerging molecules is Maxwellian both in the matter of speeds and in that of the "random distribution" of directions. This is the only case of diffuse reflection which has any physical probability and which is not in contradiction with the second law. For it Epstein obtains

$$F=[(4/3)+(\pi/6)]\pi\rho a^2\bar{c}v=1.857\pi\rho a^2\bar{c}v \tag{7}$$

Case D. Radial reflection. This purely hypothetical case assumes the return of all impinging molecules normally to the surface and without change of energy. Although such an ideal case is of course impossible, McKeehan,[7] Gaeda,[20] and Lenard[21] have all contended for the possibility of a *preference*, at least, of the emerging molecules for normal emission. Lenard and Epstein agree in finding for this case

$$F=(20/9)\pi\rho a^2\bar{c}v. \tag{8}$$

Now the foregoing formulas may be used for computing the value of $(A+B)$ corresponding to each particular case. Thus, it was shown above that in the limiting case of a very rare gas the resistance must be proportional to a^2. Although viscosity has nothing to do with the resistance, it is legitimate to retain, if we like, the viscosity coefficient in the resistance-constant, and hence to write for this limiting case in conformity with Eq. (2), in Case A for example, since $(A+B)$ is as yet quite undetermined,

$$F=\frac{6\pi\eta av}{1+(A+B)l/a}=(4\pi/3)\rho a^2\bar{c}v$$

Writing, then, in accordance with the convention consistently used in this work, $\eta=.3502\rho\bar{c}l$, and solving for $(A+B)$, there results, when l/a is so large that unity is negligible in comparison with $(A+B)l/a$,

For Case A : $(A+B)=1.575$
For Case B : $(A+B)=1.575$
For Case C_a: $(A+B)=1.181$
For Case C_b: $(A+B)=1.131$
For Case D : $(A+B)=\ .945$

While, then, the determination of slip-coefficient (i.e. of A) does not enable us to differentiate at all between condensation and re-evaporation,

[20] Gaede, Ann. der Phys. **41**, 323, 1913
[21] Lenard, Ann. der Phys. **60**, 372, 1919

diffuse, and radial reflection (cases *B*, *C*, and *D*, respectively), the foregoing measurements at very low pressures, combined with certain theoretical considerations, supply a precise criterion for so doing.

b. Thermodynamic considerations and Case D. It has already been pointed out by Gaede[22] that it is impossible, without a violation of the second law of thermodynamics, that the reactions on any *stationary* surface due to the molecules emerging from it, should be different from the reactions due to the molecules incident upon it. But the distribution of the *impinging* molecules is the Maxwellian and therefore follows the cosine law (diffuse incidence). Hence the reactions on a surface *at rest*, due to the emerging molecules, must also correspond to those of diffuse emergence. If this were not so, it would be possible to make surface *B* (Fig. 6), a rough one, which necessarily gives rise to diffuse emergence, and

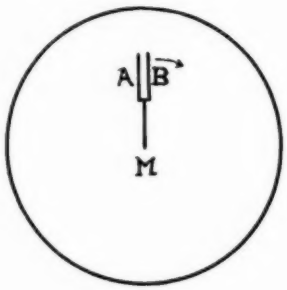

Fig. 6.

to coat *A* with a liquid or with any other substance which by hypothesis gives rise to a preferential radial emission. The incidence reactions on *A* and *B* would then be balanced, but the emergence reactions on *A* would exceed those on *B* and rotation about *M* in the direction of the arrow would result, thus violating the second law of thermodynamics. It is to be noted that this condition is not at all at variance with the existence of *specular* reflection, since such reflection gives the same distribution to the emerging and the incident molecules. *It is, however, completely at variance with the assumption that such fraction of the molecules as are absorbed and re-emitted have any tendency whatever toward normal emergence.* Gaede assumes such preferential normal emission from all *liquid* surfaces, and calls into existence his hypothetical gaseous film condensed upon his glass-surfaces, in order to make these surfaces act like a liquid in producing a preferential normal emission, a condition which he needs for one phase of his argument. He then attempts to avoid the thermodynamic difficulty which he himself has presented as

[22] Gaede Ann. der Phys. **41**, 331, 1913

in the foregoing, by assuming that the surface upon which this gas film is condensed has such a degree of *mechanical* irregularity as to re-distribute the emerging molecules in all directions. *Since, however, some of the surfaces dealt with in the present experiments are already those of liquids (oil drops), it is clearly impossible to invoke complete mechanical roughness to produce the diffuse emission demanded by the thermodynamics.* Furthermore, Gaede's assumption obviously requires that there be no differences of mechanical roughness whatever among different surfaces, but rather that all surfaces, whether liquid or solid, act like surfaces which are mechanically rough. Such an assumption is not only of improbable correctness from *a priori* considerations, but it is completely at variance with the facts of specular reflection which I have previousiy reported, and which are fortified by the results to be presented below.

It is also permissible to add that the argument given by both Gaede and Lenard in the endeavor to render intelligible from a mechanical viewpoint the assumed radial emission from a liquid surface is, as it seems to me, invalid. That argument is that in view of the forces existing near the surface, the molecules which attempt to escape obliquely are more likely to be pulled back into the surface than are those which escape near the vertical and that therefore the emission is primarily in the direction of the vertical. But I think it more correct to say that although it is true that the molecules which *start* to emerge near the normal are the only ones which can escape, yet the action of the normal surface-force must result in the distribution of the angles of emission of these molecules in all directions by the time they succeed in getting through.[23] Indeed, this is demanded by the Maxwell Distribution-Law which as is well known, holds as well for the molecules emerging from a liquid surface as for those on either side of the surface; for the Maxwellian distribution means *random distribution of directions*, as well as a particular distribution of speeds. *In other words, from neither mechanical nor thermodynamic considerations it is possible to admit a preferential emission of molecules from any surface, liquid or solid, in the direction of the normal.* This disposes entirely of the need of further consideration of Case D, and makes it necessary to reconcile the experimental value of the constant $(A+B)$ with the types of emission or reflection represented in Cases A, B and C.

c. The elimination of Case B. The experimental value of $(A+B)$, namely, 1.154, is altogether irreconcilable with the theory of condensation and subsequent re-evaporation which is uniform over all parts of

[23] This dynamical argument against the possibility of a preference for normal emission, was first called to my attention by Mr. C. G. Darwin.

the surface (Case B). It is also irreconcilable with any combination of specular reflection with a condensation and re-evaporation of this sort, since for both of these cases the value of $(A+B)$ should be 1.57. From the results obtained by Knudsen,[24] Langmuir,[25] and Wood[26] on the reflection of the molecules of metallic vapors, it might at first be thought that Case B would be nearly realized with mercury droplets falling through the vapor of mercury, for example; for the foregoing authors find that in such cases practically all impinging vapor-molecules do suffer condensation. And both the rotation of the droplets, because of their Brownian movements, and their high thermal-conductivity, might be expected to distribute the emitted molecules more or less uniformly. However, Epstein shows in his paper that when the impacts are as infrequent as is the case for very large values of l/a, even a substance like oil behaves as a perfect conductor of heat, so that the high conductivity of metallic droplets would not cause them to behave any differently in this respect from the oil droplets. Also, since the observed value of $(A+B)$ for oil shows that the Brownian movements of the oil drops have in fact no appreciable effect in distributing the emerging molecules uniformly, they could not do so in the case of metals either. It appears then, in view of Epstein's analysis combined with the foregoing experimental results, that Case B may be definitely eliminated for all kinds of drops. This leaves only A and C to consider.

d. The combination of Cases A and C. As indicated in the foregoing, the observed value of $(A+B)$, namely, 1.154, corresponds nearly to Case C_b which should theoretically give a value 1.131. But it was shown in the preceding paper, in connection with the determination of A alone, that in the case of air and oil $10\frac{1}{2}$ per cent of the molecules of the air suffer specular reflection from the surface of the oil. Computing then, from Case A the value of $(A+B)$ due to $10\frac{1}{2}$ per cent of specularly reflected molecules and $89\frac{1}{2}$ per cent of diffusely reflected ones, we find as the theoretical value of $(A+B)$, 1.164 in place of the observed value 1.154. *The agreement is probably within the limits of experimental error and furnishes excellent confirmation of the existence of specular reflection.*

It is interesting that the observed value is, if anything, a trifle lower rather than higher than the computed value. There is but one cause which could push it down, and this should have but a very minute effect with liquid spheres, but it is of importance to consider it because of a later application. The whole resistance F to the motion of the sphere

[24] Knudsen, Ann. der Phys. **47**, 697, 1915
[25] Langmuir, Phys. Rev. **8**, 149, 1916
[26] Wood, Phil. Mag. **30**, 300, 1915

arises from the difference in the number of impacts which the surrounding molecules make upon the *front* half of the sphere and those which they make upon the back half. If, then, there are any *mechanical* irregularities of any kind on the surface of the sphere, it is clear that the faces of the protuberances which are turned toward the direction of motion, are going to be hit by molecules more frequently than are those which are turned away from it, so that even if each element of the surface reflects diffusely, the total momentum transferred to the sphere by the excess of molecules which impinge on the front face, is somewhat larger, by virtue of these mechanical irregularities, than it would be if the surface were perfectly spherical and each point reflected diffusely, as was assumed in the working out of Case C_b. In other words, even with each element of the surface reflecting diffusely, any sort of mechanical irregularities, however slight, would tend to increase the resistance and therefore to produce a value of A smaller than 1.164. It is possible that this effect may be responsible for the slight difference between 1.154 and 1.164.

e. Significance of the term diffuse reflection. Although the results herewith obtained are apparently quite unambiguous in demonstrating that a law of reflection corresponding closely to Case C_b is the correct one, it is to be particularly emphasized that the method here used is incapable of distinguishing between diffuse reflection without interchange of energy with the surface, and condensation and re-evaporation *of such sort that each element of the surface re-evaporates all of the molecules which fall upon it.* The distinction between these two cases can only be made by measurements upon the flow of heat through these surfaces. In other words, no definite conclusions with regard to the value of "accommodation coefficients"[27] can be drawn from measurements upon $(A+B)$. It is, of course, true that specular reflection, such as has been here found, necessarily means an accommodation coefficient less than 1, since specular reflection undoubtedly means the return of molecules after a single impact. The fraction of the molecules which are not specularly reflected, however, may be thought of, so far as these experiments are concerned, either as "condensed and re-evaporated from the same spot," or as "diffusely reflected." The fact that they must be re-evaporated from the same spot (for the number of incident molecules varies from a maximum in front to a minimum behind) seems to make the term "diffuse reflection" more appropriate, while the fact that the distribution of the emergent molecules is the Maxwellian and therefore is determined by conditions existing on the sphere itself and not by the conditions of

[27] See Smoluchowski, Wied. Ann. **64,** 101, 1898; Phil. Mag. **46,** 199, 1898; and Knudsen, Ann. der Phys. **34,** 593, 1911

incidence (for, on account of the motion of the sphere, the distribution of the incident velocities is not Maxwellian) seems to make the designation condensation and re-evaporation more appropriate.

5. General Validity of the Foregoing Law of Fall

It was pointed out in the preceding paper that with an oil surface, the value of A varies from .815 for hydrogen to .90 for helium, these figures corresponding to a variation in the percentage of specular reflection from 7.5 in the case of hydrogen to 12.6 in the case of helium. It might at first be thought that such changes in the percentage of specular reflection would exhibit themselves as considerable differences in $(A+B)$, but the working out of the actual numerical values by the method just employed shows that a combination of $7\frac{1}{2}$ per cent of specular reflection with $92\frac{1}{2}$ per cent of diffuse reflection, gives rise to a value of $(A+B)$ of 1.154, and the combination of 12.6 per cent of specular reflection with 87.4 per cent of diffuse reflection, corresponds to a value of $(A+B)$ only slightly greater, viz. 1.170. In other words, unless my values of $(A+B)$ are reliable to better than 1 per cent, it would be impossible to observe any differences between the theoretical values of $(A+B)$ for oil and air (1.164), for oil and helium (1.170) and for oil and hydrogen (1.154). Even in the case of shellac and air, which, according to slip-measurements shows 21 per cent specular reflection or nearly three times that found in the case of hydrogen and oil, the value of $(A+B)$ comes out but 1.197, or only a little more than 3 per cent higher than the value for air and oil. It is to be expected, too, that solid spheres of shellac will show more mechanical irregularities than would liquid spheres of oil, and this would mean that the 1 per cent of diminution of $(A+B)$ which we have attributed to mechanical irregularities in the case of oil, would presumably be larger for the shellac. *It is not then to be expected that the final resistance factor $(A+B)$ will be found to depend to any appreciable extent upon either the nature of the ambient gas or the nature of the droplet.* The recent measurements of Mr. Eglin who has repeated, at my suggestion, my measurements on oil-drops in air and has extended them to other gases, particularly the monatomic gas helium, are in excellent agreement with these predictions.

It is also interesting to observe, as will be more fully pointed out in the next section, that Knudsen's observations on glass and air lead to a value of $(A+B)$ which is within 1 per cent of the value here found for oil and air. *All of these results are important in that they show that the complete law of motion herein developed is of very general validity and can be used without fear of large error in considering the motions of any kind of*

particles in the rarefied atmosphere of the earth. It is even probable that metallic spheres would show very close to the same value of $(A+B)$ as is here found for oil.

6. Comparison with Results of Other Observers

There are two results by Knudsen with which the foregoing observations and conclusions may be compared. The first is that in which he obtained, by measuring the damping factor of oscillating glass spheres, the law of resistance represented by Eq. (4). It is interesting to observe that a part of the difference between the numerical values of his constants (A, B, and c) and mine is due to the fact that he uses a different convention in the formula for viscosity, namely: $\eta = .310\rho cl$, whereas I, merely for the sake of uniformity with my other work, have used the value .3502 in place of his .310. *When this difference is allowed for, it is found that Knudsen's value of $(A+B)$ for his glass spheres, in terms of my convention, is 1.164 which is within a trifle less than 1 percent of my value.* It is true that his value of A is more than 10 per cent lower than mine, namely, .768 while mine is .864; but it is my judgment that while Knudsen's method is reliable for obtaining the value of $(A+B)$ that is, the resistance when the gas is exceedingly rare, it is open to serious objection when the gas is dense, because of the well established retarding influence of the walls of a vessel[28] upon the motion of a sphere moving through a *viscous* medium within the vessel. I do not therefore think Knudsen's formula for the law of fall is as trustworthy as my own, but I see no reason why his value of $(A+B)$ for glass may not be about as good as mine for oil. *There is nothing but specular reflection on glass to push this value from its theoretical limit 1.13 up to its observed value 1.164.*

The second result of Knudsen's which appears at first sight to be at variance with the conclusions drawn in this and the preceding paper on the coefficient of slip, is found in the fact that both he and Gaede in their measurements upon the outflow of greatly rarified gases through capillary tubes, apparently establish the validity of the law of diffuse reflection from glass surfaces, whereas I find what seems to me to be unimpeachable evidence that there is $10\frac{1}{2}$ per cent of specular reflection under the same circumstances. Knudsen's argument rests upon the fact that when he computes the rate of flow of a gas at very low pressures through his capillary tube upon the assumption of the diffuse reflection of the molecules, he obtains a result which is within the limit of observational error of his observed rate of flow. *It should be pointed out, however, that if there*

[28] See Arnold, Phil. Mag. **22**, 757, 1911

are any mechanical irregularities in the inner surface of the glass tube, such as were assumed in a preceding section, the rate of flow at very low pressure through a capillary tube should be less than that corresponding to the law of diffuse reflection. It is quite clear that at pressures so low that the molecules, if properly directed, can shoot the whole length of the tube without making an impact, mechanical irregularities *such as must exist on the inside of the tube,* are bound to receive more impacts on the faces which are turned toward the point of high pressure than on the opposite faces, and even if the law of reflection from each element of surface is "diffuse," there is still a tendency for these protruding irregularities to throw back the molecules in the direction from which they came and therefore to give rise to a rate of flow which is *less* than that corresponding to diffuse reflection. Gaede[22] points this out with great clearness when he is picturing these mechanical irregularities as covered with a film of gas, but he seems to forget that the same reasoning holds equally well when there is no film of adhering gas.

In a word, then, if Knudsen and Gaede obtain at sufficiently low pressures a rate of flow through tubes which is in agreement with the law of diffuse reflection, *the result can only be interpreted as meaning that there was in their experiments a tendency toward specular reflection from the glass which increased the rate of flow by just such an amount as to neutralize the retarding effect of the mechanical protuberances here under consideration. In other words, even Knudsen's results seem to call for specular reflection for their proper interpretation.*

It is to be noted that this phenomenon of a general return of the molecules after impact in the direction from which they came, in the case of flows through capillary tubes, will theoretically begin to diminish when the mean free path becomes smaller than the length of the tube, and that it will become less and less appreciable as the mean free path becomes smaller and smaller in comparison with the dimensions of the tube, disappearing entirely when the conditions of viscous flow have set in, for then the mean free path has become very minute and the velocity in the layer next the outside wall has become completely negligible in comparison with the molecular velocity. The lower theoretical value of A should then be that corresponding to diffuse reflection, viz: $A = .7004$, as computed in a preceding paper.

The very marked minimum which Gaede found in "G" when he was measuring the outflow of gas *in a thin sheet* instead of through a circular cross section, and which was reached at the high value of the pressure of 23 mm, probably has its explanation in the changing of the stream lines within the vessel as the flow changed from one governed by the

laws of viscous flow to one governed by the laws of molecular flow. *It is particularly significant that Gaede reports no such marked minimum when he worked with a cylindrical vessel, that is, one which is symmetrical with respect to the axis of flow.* In that case he found only a slight tendency toward a minimum, as Knudsen had done before him. This may have its cause in the effect just mentioned, which should persist to some extent even in tubes of circular section, or it may be due, as Knudsen suggested, to water vapor or other residual gases.

The present results remove entirely such discrepancy as seemed to exist between my original results on the correction of Stokes' law and those of McKeehan, whose value of A came out some 15 per cent higher than mine. Since some of McKeehan's results were taken at relatively high values of l/a, his large A is in reality a mixture of the present constants A and $(A+B)$, the precision of his measurements not being sufficient to bring to light the two slopes which actually exist.

I wish to thank Dr. Yoshio Ishida for his assistance in the experimental portion of this investigation.

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THE DISTRIBUTION OF INTENSITY IN THE BROADENED BALMER LINES OF HYDROGEN

By E. O. Hulburt

Abstract

Broadening of the Balmer lines of hydrogen by condensed discharges.—(1) At various pressures, 48 to 250 mm, the intensity distribution was determined for $H\beta$, $H\gamma$ and $H\delta$ by photographing the spectra through a neutral wedge. In each case the broadening was symmetrical, amounting to about 60A for each line at 250 mm, but the curves gave evidences of structure characteristic of each line. The effect of a quenched gap in series with the tube was to increase the broadening, while inductance decreased it. (2) *In mixtures with He or* N_2, the broadening was the same as in hydrogen alone at the same total pressure. (3) *Stark theory of broadening* which relates it to the Stark effect of the electrical fields of the ionized atoms or the radiating atoms, *is given mathematical formulation* by assuming a probability law for the distribution of the atoms and ions and an inverse square law for the strength of the field, and introducing Sommerfeld's quantum expression for the Stark displacement. This gives $\log I_\lambda = \log [a/(\lambda_0-\lambda)] - b/(\lambda_0-\lambda)$, where $a = A\lambda\lambda_0 p^2 f$ and $b = B\lambda\lambda_0 p^{2/3} f$, where f is a known function of the quantum numbers. Comparison with experiment shows agreement as to the general form of the distribution curves. The great broadening produced by the condensed discharge is then due to the momentary high current density and corresponding large proportion of ionized atoms.

Neutral wedge cell, filled with an aqueous solution of a black dye, was found more convenient to adjust than the ordinary neutral glass wedge.

Introduction

UNDER usual excitation by a transformer or induction coil the lines of the Balmer series of hydrogen at low pressure are sharply defined although weak in intensity. When the gas pressure is increased to several hundred mm of mercury and when condensed discharges are employed, the Balmer lines increase in intensity and widen until almost unrecognizable. This broadening has received unusual attention from investigators because of the large magnitude and because of the importance of the hydrogen atom in theories of atomic structure. However, Rossi[1] seems to have been the first to indicate what now appears to be the true cause of the enhancement of the lines. As a result of his observations he stated, "It would seem that current density is a very important, if not the only,

[1] Rossi, Astrophysical Journal **40**, 232, 1914

factor in the phenomenon." The work of Stark on the modifications of radiations when the source of the radiations was subjected to an electric field, led to the suggestion that the broadening of spectrum lines might in some instances be attributed to the presence of electric charges in the vicinity of luminous atoms. This suggestion was given definite form by Merton[2] and by Nicholson and Merton[3] in an investigation of the intensity distribution across $H\alpha$, $H\beta$ and $H\gamma$ radiated from hydrogen at atmospheric pressure when excited by condensed discharges. A detailed analysis of the intensity curve of $H\alpha$ enabled them to conclude that the broadening was in close agreement with the results to be expected from Stark's observations of the electrical resolution of the line.

It seemed that an application of the recent theoretical work on the Stark effect of the Bohr hydrogen atom to the broadening problem would lead to a clearer understanding of the phenomenon. This has been attempted in the present investigation. After the intensity distribution had been measured across the hydrogen lines $H\beta$, $H\gamma$ and $H\delta$, stimulated by condensed discharges, for a pressure range from 48 to 250 mm of mercury, theoretical consideration of the radiations to be expected from a gaseous system of hydrogen atoms of the Bohr design mingled with charged particles, yielded a formula which gave substantial agreement with the observed intensity curves.

Experimental Details

Pure dry hydrogen, prepared from hydrochloric acid and zinc, was passed into the end-on discharge tube *d*, Fig. 1, made of glass with

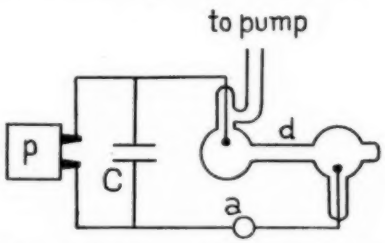

Fig. 1. Discharge tube and connections.

aluminum electrodes arranged out of line with the capillary, which was 4 cm long and 5 mm in diameter. The gas was excited by the discharges from a condenser *C* of capacity 0.0084 microfarads which received its power from a 1 kw, 25 kv, transformer *P*. The current through the tube was read by the thermo-galvanometer *a*. The current was in all cases

[2] Merton, Proc. Roy. Soc., **92**, 322, 1915
[3] Nicholson and Merton, Phil. Trans. Roy. Soc., **216**, 458, 1916

oscillatory, of frequency about 0.67×10^6 per second as measured by a wave-meter. The spectra were photographed with a glass prism spectroscope of the Littrow type, the dispersion at 5000, 4000, and 3600A being about 40, 20, and 15A per mm, respectively.

To obtain the distribution of intensity across the line a neutral wedge was placed before the slit of the spectrograph. A complete description of the neutral wedge method and a discussion of the theory is found in the papers by Merton, already referred to, in which the advantages and possibilities of the method and the precautions to be observed are clearly set forth. In the present instance a wedge was constructed by cementing glass plates together with sealing wax to form a cell with two wedge shaped compartments, Fig. 2. The angle α of the wedge was 17°, and the external dimensions of the cell were $1.5 \times 2.5 \times 3.5$ cm. One compartment

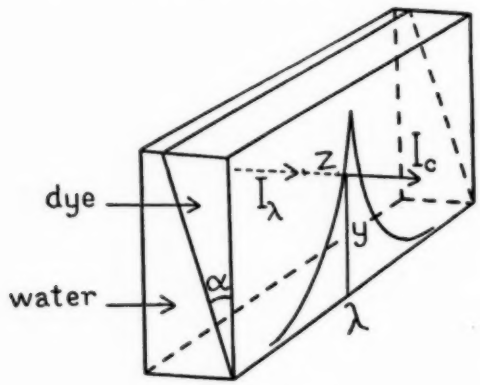

Fig. 2. Wedge cell.

was filled with water and the other with an aqueous solution of a black dye ("Erie Black, G×OO," National Anilene and Chemical Co., New York). The concentration of the solution was varied until the photographs had the best appearance. The advantage which this type of wedge had over a neutral glass wedge lay in the ease of construction and the freedom of adjustment to the experimental conditions.

The neutral wedge method. When the neutral wedge is interposed between a spectral line of finite width and the photographic plate, let us suppose that the plate records an image of the line of the form shown, for illustration, in Fig. 2. This figure indicates that the wedge was contiguous to the plate, whereas in reality the wedge was in front of the slit of the spectrograph, but the two cases are of course identical so far as the present discussion is concerned. We now seek the determination of the true intensity distribution curve of the line from the photographic

image found by means of the wedge. At all points on the edge of the image the intensity of the light has a constant value I_c, since under the condition of the exposure, light of less intensity does not produce a perceptible effect on the photographic plate. Let the coordinates of a point on the contour of the image be (λ, y), where y is measured from the thin edge of the wedge. Let z be the thickness of the wedge at this point. If I_λ is the undiminished intensity of the light of wave-length λ at this point, $I_c = I_\lambda e^{-kz}$, or

$$I_c = I_\lambda e^{ky \tan \alpha}, \qquad (1)$$

where k is the absorption coefficient of the material of the wedge for radiation of wave-length λ. I_c is a constant, and we shall assume k is a constant throughout the range of wave-lengths of the broadened line. Therefore from (1) the values of I_λ in arbitrary units may be determined for each value of λ merely by measuring y for each λ, and in this way the true intensity distribution curve may be obtained. Actually in the present experiment a variation of this procedure has been adopted; namely, I_λ was determined as a function of λ throughout the line from a theoretical consideration. From this function the form of the intensity distribution curve to be expected after the spectral line had passed through the wedge was calculated by means of (1) and a comparison was then effected between the theoretical and the experimental intensity curves.

Experimental Results

Spectra of hydrogen were photographed through the neutral wedge for pressures 48, 112, 160 and 250 mm of mercury. These are shown in Plate 1, *a*, *b*, *c* and *d*, respectively. The currents through the gas for each pressure were 1.2, 2.3, 2.8 and 4.1 amperes, respectively. The time of exposure was 20 minutes in each case. The contour of the image of the lines was in general convex to the wave-length axis for all the lines, the curves as seen in the reproduction being fairly smooth. On the original plates, however, the contours gave unmistakable evidence of structure in the line. $H\beta$ was noticeably a close hazy doublet at the apex; $H\gamma$ and $H\delta$ gave evidences of slight wings symmetrically placed on either side; and $H\gamma$ exhibited a bright central core which was lacking in the case of $H\delta$. These details are indicated more clearly in the heavy line drawings in Fig. 3 of the images for a pressure of 250 mm reduced to a uniform scale of wave-lengths. The facts concerning the structure of $H\beta$ and $H\gamma$ when broadened have been mentioned before.[1,2] If the images of $H\beta$ and $H\lambda$ were enlarged until their highest ordinates were equal to the maximum ordinate of $H\alpha$ it would be seen that the widening for a specified pressure increases with the series term number of the line.

THEORETICAL

We proceed to a consideration of the simple theory of the general form of the curves and reserve for a later paragraph a suggestion for a more detailed explanation.

Intermingled with the radiating hydrogen atoms in the discharge tube are charged particles. These charged particles may be electrons, ions or even the component charges of a neutral atom. As a result the radiating atom finds itself in an electric field and therefore, in agreement with the observations of Stark, instead of emitting a single line it gives forth a group of lines whose displacement from the parent line is directly

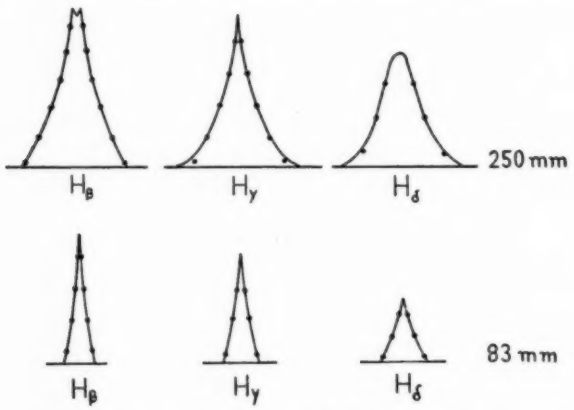

Fig. 3. Broadening curves; observed (full lines) and computed (dots).

proportional to the strength of the electric field. Throughout a finite interval of time a radiating atom may be expected to be subjected to fields of a wide range of intensities and in spite of the many complexities of the case it seems reasonable to suppose that the average over a considerable length of time of the influence of the electric fields on a large number of radiating atoms will be in accordance with a probability law. In the following paragraphs these ideas are couched in mathematical terms.

The hydrogen gas in the path of the condensed discharges is largely atomic and is composed of electrons and of charged and neutral, luminous and quiescent atoms. Since ionization is probably essential to luminosity under the conditions of the discharge we cannot be far wrong in assuming that the number of luminous atoms and the number of the charged particles are of about the same order of magnitude. J. J. Thomson[4] has estimated the ratio of the number of ions to the total num-

[4] Thomson, "Conduction of Electricity Through Gases," 1906, p. 83

ber of molecules in a gas during the passage of an electric current to be about 10^{-14} in a certain instance. In the present experiment this ratio was probably much greater, because condensed discharges were used, but we may estimate with safety that the ratio was not greater than, say, 10^{-6}. The conclusion is that the number of both luminous atoms and charged particles was small compared to the total number of atoms present.

Let the total number of atoms per unit volume be ν, of which a fraction q contribute to the radiation. Let the distance from a luminous atom to a charged particle be denoted by δ. It is assumed that the number of luminous atoms ν_1 per unit volume which are at a distance δ from a neighboring charged particle, is given by the probability relation[5]

$$\nu_1 = A\nu\delta^2 e^{-B\delta^3}. \tag{2}$$

In order to avoid needless complication we simplify matters by assuming that the luminous atoms are the charged particles. This does not materially affect the argument because we are interested in the orders of magnitude of the numerical constants and not in their precise values. On this assumption we may write $\int_0^\infty \nu_1 d\delta = q\nu$; hence, $A = 4q\sqrt{B^3/\pi}$. If δ_m is the average distance between luminous atoms, then

$$\delta_m = 4\sqrt{\frac{B^3}{\pi}} \int_0^\infty e^{-B\delta^3} \delta^3 d\delta = \frac{2}{\sqrt{\pi B}}.$$

Also $\delta_m^3 = 1/q\nu$. Therefore $A = 2^5 q\nu/\pi^2$ and $B = 4q^{2/3}\nu^{2/3}/\pi$. ν depends on the pressure and may be written $\nu = 4\times 10^{19} p/760$, where p is the pressure in mm of mercury. Introducing these values into (2) leads to

$$\nu_1 = \alpha p^2 \delta^2 e^{-\beta p^{2/3}\delta^3}, \tag{3}$$

where $\alpha = 2^5/\pi^2 \left(\frac{4\times 10^{19}}{760}\right)^2 q$ and $\beta = 4/\pi \left(\frac{4\times 10^{19}}{760}\right)^{2/3} q^{2/3} = 5\times 10^{11} q^{2/3}$.

Making use of the estimated maximum value of q, i.e. 10^{-6}, the maximum value of β does not exceed 10^7.

The experiments of Stark[6] have demonstrated that in the case of the Balmer lines of hydrogen the displacements of the Stark components are closely proportional to the strength of the electric field. In his theoretical treatment of the electrical resolution of the radiations from the Bohr model of the hydrogen atom Sommerfeld[7] has derived a general

[5] Jeans, "Dynamical Theory of Gases," 1904, p. 28
[6] Stark, Ann. der Phys. **48**, 193, 1915
[7] Sommerfeld, "Atombau und Spektrallinien," 1922, p. 357.

relation for the displacement of any component, which is in agreement with Stark's data, namely,

$$\lambda_o - \lambda = \frac{3hF}{8\pi^2 mE} \frac{\lambda\lambda_o}{c} f, \tag{4}$$

where f is a function of the quantum numbers. The exact value of f is known; it differs for each component. λ_o is the wave-length of the parent line; λ is the wave-length of the component when the intensity of the electric field is F; h is the Planck constant; m the electronic mass; E the nuclear charge, and c is the velocity of light in vacuum. Since the Stark components are symmetrically placed and equally displaced on either side of the parent line the absolute value of $\lambda_o - \lambda$ is used in (4). In the problem under discussion the luminous atom is conceived to be subjected to the electric field of the charge e on the neighboring atom a distance δ away. The strength of the electric field is e/δ^2, the dielectric constant of the medium being unity, and if δ is large compared to the diameter of the atom the field is approximately uniform over the luminous atom. We thereupon replace F by e/δ^2 in (4) and solve for δ^2. This yields $\delta^2 = \alpha'/(\lambda_o - \lambda)$, where $\alpha' = 3he\lambda\lambda_o f/8\pi^2 mEc$. Taking f to be of the order of 10 and putting $\lambda = \lambda_o = 5000$A, we find α' to be of the order of 10^{-11}. Upon substitution of the expression for δ^2 in (3) we obtain

$$\nu_1 = \frac{\alpha\alpha' p^2}{(\lambda_o - \lambda)} e^{-[\beta\alpha' p^{2/3}/(\lambda_o - \lambda)]}. \tag{5}$$

It must be noted that in equating F to e/δ^2 we have tacitly assumed that the field was due to a single charge. Actually the electric field at any point in the gas was the resultant of the fields of a swarm of charged particles of both signs in the vicinity of the point. This indicates that the right hand side of (5) and the exponent should each be multiplied by some fraction.

We may now assume that the intensity I_λ of the radiations of wave-length λ is proportional to ν_1, and write $I_\lambda = \alpha''\nu_1$. Hence from (5)

$$I_\lambda = \frac{\alpha\alpha'\alpha'' p^2}{(\lambda_o - \lambda)} e^{-[\beta\alpha' p^{2/3}/(\lambda_o - \lambda)]}. \tag{6}$$

The quantity $\beta\alpha' p^{2/3}$, according to our numerical estimates of β and α', is a small quantity, certainly never greater than 1/10 for pressures of the order of one atmosphere, and probably much less. We may therefore replace the exponential term of (6) by unity without appreciable error unless the absolute value of $\lambda_o - \lambda$ expressed in angstrom units be less than 1/10. Eq. (6) then becomes, to a close approximation,

$$I_\lambda = gp^2/(\lambda_o - \lambda), \tag{7}$$

where $g=\alpha\alpha'\alpha''$ and is approximately a constant across the broadened line. From (7) the line may be expected to widen with pressure. When I from (6) is plotted in arbitrary units against λ a curve of the form given by the heavy line of Fig. 4 is obtained. The curve is obviously not drawn to scale. At λ_o, I_λ is zero and the distance apart of the maxima is less than 0.1 A. This crevice in the intensity curve is perhaps beyond the reach of detection by experiment, and probably is of no physical significance. It merely results from the refusal of Eq. (6) to admit the possibility of there being any atom at all which emits the unaffected wave-length λ_o. In regard to the approximate formula (7), the intensity curve conforms closely to that of formula (6) except n the small interval

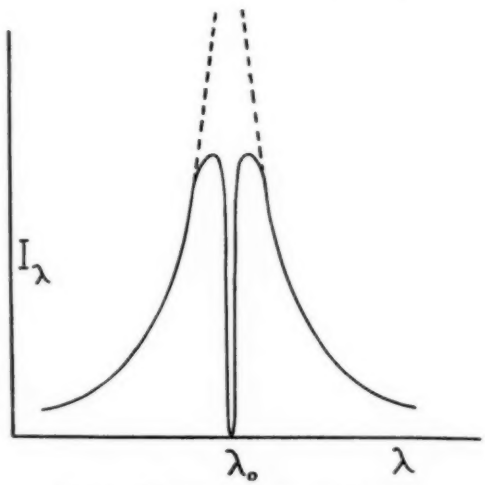

Fig. 4. Theoretical broadening curve.

between the two maxima in which the approximate formula is invalid. Ignorance of the exact physical conditions renders it difficult to attempt to derive an expression for the intensity at wave-length λ in terms of the intensity at the center of the parent line. We content ourselves therefore with formula (7) which affords relative values of I_λ for regions neither too near nor too remote from λ_o.

It remains to determine the equation of the intensity curve after the light has traversed the neutral wedge. This is obtained by eliminating I_λ between (1) and (7). There results

$$\lambda_o-\lambda=(gp^2/I_c)e^{-ky\tan\alpha}. \tag{8}$$

Comparison Between Theory and Experiment

Drawings of the enlarged images of the lines were made and reduced to a uniform wave-length scale. These are shown by the full lines of Fig. 3

for $H\beta$, $H\lambda$, and $H\delta$ at pressures 250 and 83 mm, which were plotted with values of y in arbitrary units as ordinates against values of $\lambda_o - \lambda$ in angstrom units as abscissas. The constants g/I_c and $k \tan \alpha$ of Eq. (8) were determined from two observed points on the contour of $H\beta$ at a pressure 250 mm, and points on the intensity curve were then calculated. To obtain the theoretical curves for the other lines and pressures it was only necessary to readjust the quantity g/I_c of Eq. (8). This was permissible because the intensities were in arbitrary units. The calculated points are shown by the dots of Fig. 3. Similar comparisons were affected for all the other lines, and in all instances good agreement was found between the general forms of the observed and theoretical intensity curves.

Structural detail in the broadened line. The theoretical ideas thus far advanced in explanation of the general form of the intensity curve will not suffice to account for the evidences of structure observed in the broadened lines. A more detailed consideration is necessary. Merton[2] has supplied this by drawing attention to the close correspondence between the Stark components of a line and the form of the intensity distribution curve. To show this the p and s components of the electrical resolution of $H\beta$, $H\lambda$ and $H\delta$ as determined by Stark[8] are given in Fig. 5. It needs only a glance at these components to see that the $H\beta$ radiations

Fig. 5. Stark effect components.

from a large number of hydrogen atoms subjected to a wide range of electric fields will result in a widened line with perhaps a weak minimum at the center. In the cases of $H\lambda$ and $H\delta$ we should expect a widened line with more or less prominent wings, the center of $H\lambda$ being more brilliant than the center of $H\delta$. As far as can be judged these conclusions are in agreement with the appearance of the photographic images of the lines.

The role of the condensed discharge. As an outcome of the views set forth in explanation of the broadening, we are led to an understanding of the role played by the condensed discharge. In the condensed discharge the current density is very great for a short interval of time at the commencement of the discharge. It may easily amount to several hundred amperes. A gas which is stimulated by such a discharge emits

[8] Sommerfeld, loc. cit., p. 357

radiations characteristic of those caused by the passage of heavy currents. The luminous atoms in such a case are in the midst of a vast number of charged particles and a relatively large number may be expected to be subjected to strong electric fields. This results in the widening of the lines. On the other hand if a steady current, either direct or alternating, traverses the gas the current density never attains very high values and the charges present in the gas are never very numerous. Therefore the luminous atoms rarely experience strong electrical fields and no marked broadening of the lines occurs.

The effect of the quenched gap. The photographs *e* and *f* of Plate I indicate the increase in width of $H\beta$ occasioned by the introduction of a quenched gap in series with the tube. The pressure of the hydrogen was 130 mm, the current 2.1 amperes and the time of exposure 20 minutes in each case. For *e* the quenched gap was used, for *f* the discharge took place directly through the tube without the gap. The effect of the gap in producing widening was more marked at the lower than at the higher gas pressures. The insertion of the gap enabled the charges to accumulate on the condenser plates to higher potentials, so that when the discharge occurred a greater current than otherwise passed through the tube. The current was rapidly damped by the quenching action of the gap. As a consequence the gas was stimulated at each discharge by abrupt pulses of current more intense than those which occurred without the gap, even though the currents read by the thermogalvanometer were the same in the two cases. The stronger current pulses produced the greater broadening. The reason that the gap produced less effect for high gas pressures was simply that in those cases the tube itself quenched the discharge to a greater extent.

The effect of inductance. A coil of inductance 2.2×10^{-5} henries in series with the discharge tube reduced the widths of the broadened lines. An illustration of this is afforded by the photographs *g* and *h* of $H\beta$, *g* taken with the coil and *h* without the coil. The current was 3.0 amperes, the gas pressure 140 mm, and the time of exposure 11 minutes in each case. The frequency of the oscillatory discharge with the inductance was 1.2×10^{5} and without it was 6.7×10^{5}; these were measured with a wavemeter, the tuning being of course very broad because of the resistance of the tube. The inductance served to distribute the discharge over a longer interval of time so that the pulses of current were of less intensity and therefore the spectrum lines were narrower than when the inductance was absent. The fact that an inductance will reduce or suppress entirely certain lines excited by spark discharges, has been known for a long time, but it appears that in some instances the electrical conditions of the

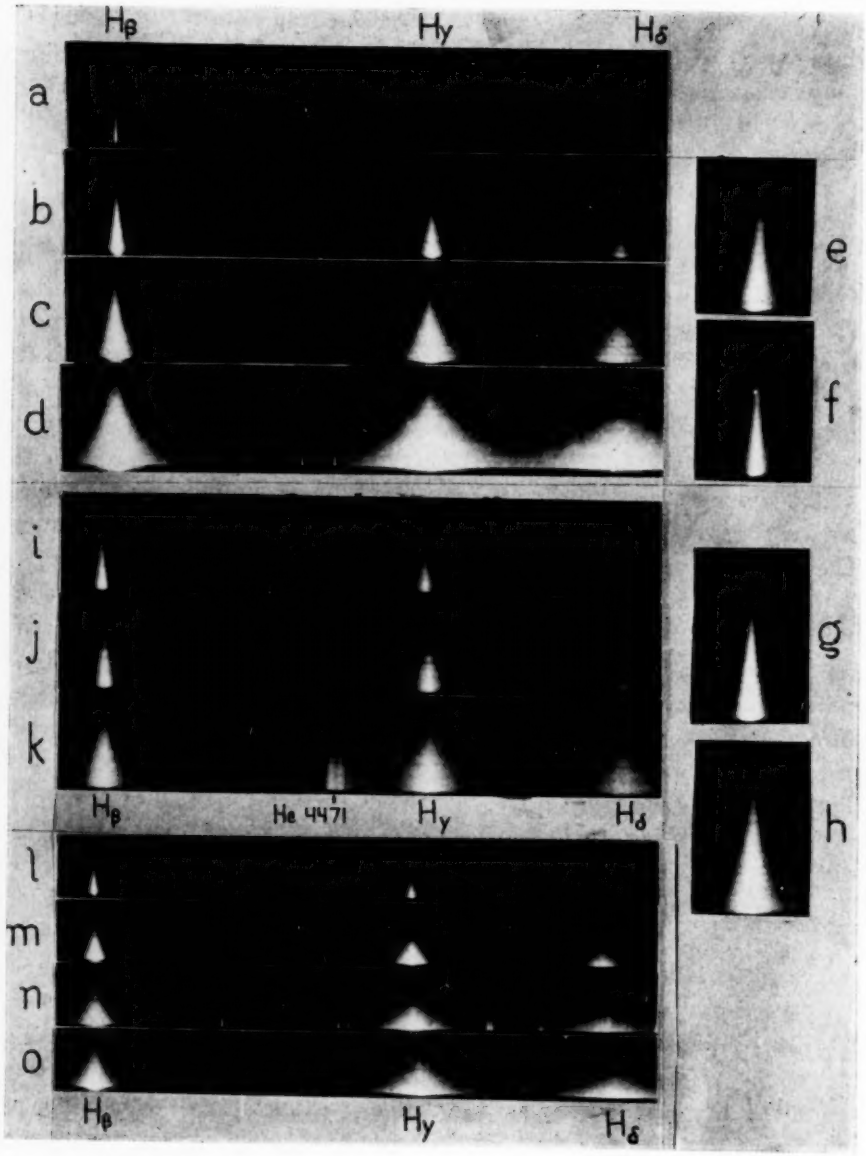

Plate I. Broadening of the Hydrogen lines by condensed discharges.

experiments have not been described in sufficient detail to enable possible explanations to be advanced.

Mixtures of Hydrogen with Helium and Nitrogen

Mixtures with helium. It was found that the Balmer lines of hydrogen at a relatively low pressure were broadened when the pressure was increased by the addition of an inert gas such as helium or nitrogen, in the same manner as by the addition of more hydrogen. Photographs *i*, *j* and *k* show the effect of helium. The data for these photographs are given in Table I. The helium contained a trace of nitrogen but this probably

TABLE I

Data for photographs i, j, and k

	Pressure of hydrogen	Pressure of helium	Current	Time of exposure
i	29 mm	79 mm	1.2 amp.	20 min.
j	29	188	3.0	20
k	29	380	4.2	20

had no effect in the present experiment. The enhancement of the hydrogen lines caused by the helium was to be expected from the views already outlined. Several factors, however, must be considered. The introduction of the inert gas increased the break-down potential of the discharge tube. A violent discharge thereupon ensued and a great number of charged particles were produced in the luminous gas with consequent enhancement of the Balmer lines. The charged particles came apparently from ionized hydrogen rather than from helium, since even with partial pressures of 380 mm of helium and only 29 mm of hydrogen the helium lines were of less intensity than the hydrogen lines. This of course was to be ascribed to the high resonance and ionization potentials of helium as compared with those of hydrogen, and to the fact that the higher the ionization potential of an element the greater is the difficulty with which it can be excited to emit its line spectrum.[9]

Mixtures with nitrogen. The enhancement of the Balmer lines from hydrogen mixed with nitrogen is shown by photographs *l*, *m*, *n* and *o*. The flatness of the contours of these lines resulted from the use of a neutral wedge of greater optical density than the one used for the other photographs. The conditions under which these were taken are given in Table II. It is interesting to notice the striking similarity of photographs *n* and *o* which were taken with the same total pressures but with quite different partial pressures of the component gases. The ionization potential of nitrogen is somewhat above that of hydrogen. Some of the

[9] Saha, Phil. Mag. **41**, 268, 1921

resonance potentials, however, are slightly lower than those of hydrogen and therefore it might be supposed that the nitrogen lines would appear nearly as prominently as the hydrogen lines. This does not seem to be the case in this experiment as indicated by spectrogram *k*. However, little can be said with certainty on this point because there is no criterion for the relative intensities of the spectrum lines of different elements.

Of the possible causes of broadening of spectrum lines recognized at the present time only two seem to be of sufficient potency to effect the relatively large widening noticeable in many enhanced lines. These two causes are the electric and magnetic fields. In the present experiments

TABLE II

Data for photographs l, m, n, o

	Pressure of hydrogen	Pressure of nitrogen	Current	Time of exposure
l	85 mm	0 mm	2.3 amp.	20 min.
m	85	55	2.5	20
n	85	115	3.0	20
o	200	0	3.0	20

as well as in all usual cases of broadened lines the Zeeman effect may be ruled out, although it may be possible to devise conditions in which the Zeeman effect is operative. This suggests that the Stark effect is the cause of most cases of broadening of spectrum lines, or more precisely, that the broadening is due to the electric fields of the charged particles which are produced by the same vigorous stimulation which brings into existence the broadened line. The results of many experiments, among which may be mentioned those of Hemsalech and de Gramont,[10] point to this conclusion.

I take pleasure in thanking Dr L. I. Shaw of the Bureau of Mines for a gift of helium.

PHYSICAL LABORATORY,
UNIVERSITY OF IOWA,
January 14, 1923[11]

[10] Hemsalech and Gramont, Phil. Mag. **43**, 287 and 834, 1922

[11] The paragraphs dealing with the effects of a quenched gap and of inductance were added February 7, 1923.

CONTINUOUS SPECTRAL ENERGY DISTRIBUTION WITHIN THE X-RAY TUBE

By Paul Kirkpatrick

Abstract

Continuous spectral energy distribution of x-radiation as emitted from the target of a Coolidge tube at right angles to the beam of electrons, has been determined from the distribution curve obtained with a rock salt crystal spectrometer and a methyl iodide ionization chamber, by applying the following *corrections:* (1) For superposed higher orders (determined from polychromat curves and also from the absorption of the complex rays in aluminum); (2) for incompleteness of absorption in the ionization chamber (determined by absorption experiments); (3) for absorption by glass wall, by air, and by aluminum window (determined by observation or by computation); (4) for reflecting power of the rock salt crystal (obtained from curve derived from results of various investigators). The final curves show maxima at 0.445 and 0.503A for 71 and 51 kv respectively. Comparison of these curves with those given by the theories of Behnken, March, and Davis, shows agreement with none. The maxima correspond to the equation $\lambda_m = k + k'\lambda_o$, where λ_o is the quantum wave-length.

Intensities of various orders of x-ray spectra simultaneously reflected from a crystal, determined experimentally as stated above, do not correspond to Dauvillier's assumption. Families of spectra may be corrected for order effects by a graphical method based upon the linearity of isochromats.

Production of constant potential x-ray spectra with alternating voltage by use of a synchronous shutter between tube and spectrometer is described.

Introduction

ORDINARY x-ray spectrum curves (curves of ionization against wave-length) do not represent the actual energy distribution in x-ray emission, the curves being affected by superposition of orders, by absorption in the target, tube wall, ionization chamber window, air, etc., and by the wave-length variation of crystal reflectivity, ionization chamber absorption, and energy required for ionization. Some or all of these effects have been recognized by various workers and attempts have been made to apply the required corrections and so to learn the true form of the spectral energy curve at the origin of emission, a matter of importance.

Dauvillier[1] shows curves corrected for order, ionization chamber, and tube wall effects. March[2] has applied a tube wall correction to his (theo-

[1] Dauvillier, Ann. de Physique **13,** 49, 1920
[2] March, Phys. Zeit. **22,** 429, 1921

retical) curves. Kustner[3] shows curves corrected for the calculated effects of various crystals. Wagner and Kulenkampff[4] and Kulenkampff[5] have recently published corrected spectra for low voltage ($\lambda_o = 1.17$A).

The present paper describes the correction of spectra for from 50 to 70 kv, and the final curves set forth the wave-length energy distribution within a Coolidge x-ray tube, the measure of the energies being the amount of L, M, etc. ionization produced on complete absorption in methyl iodide vapor. The paper further presents a comparison of the corrected curves with curves resulting from three theories of continuous x-ray emission.

Apparatus and Operation

The experimental equipment consisted of a seven-inch, medium-focus, tungsten-target, Coolidge tube energized from a 2 kw transformer and 1 kw motor-generator set, the motor being operated from storage batteries at about 100 volts. The spectrometer was furnished with an accurate ten-inch circle and with microscopes reading to minutes, and carried a 41 cm ionization chamber, capable of rotation on ball bearings about the axis of the spectrometer and having a string electrometer rigidly fixed at its outer end. A rock salt crystal was used, being mounted for face reflection from the (100) planes. The x-ray beam was defined by a tube slit 18 cm from the crystal axis and an ionization chamber slit at a like distance. A third slit 4 cm from the crystal on the tube side further limited the breadth of the beam, requiring it to fall at all times within the limits of the crystal face.

Although alternating potential was applied to the tube, constant potential conditions were simulated through the introduction between the tube and the spectrometer of a *synchronous shutter* carrying a slit capable of adjustment so that only x-rays generated by a potential band of the desired width and phase should pass to the spectrometer. The shutter was of pendulum type operated by a taut steel wire attached to a pin mounted eccentrically in the end of the motor-generator shaft. The operation of the shutter at thirty oscillations per second was extremely steady. Its phase relationship to the generating potential was readily checked by observing with the spectrometer the shortest wave-length transmitted. In obtaining the spectra the phase of the shutter was so adjusted as to transmit only rays generated by the peak of the secondary voltage wave, and the width of its slit was such that the maximum possi-

[3] Kustner, Zeit. für Phys. **7**, 2, 1921
[4] Wagner and Kulenkampff, Ann. der Phys. **68**, 369, 1922
[5] Kulenkampff, Ann. der Phys. **69**, 548, 1922

ble variation in the generating voltage, assuming a sinusoidal wave-form, was one per cent. The current through the tube was held constant throughout the spectra observations, by means of a mercury rheostat of special design[6] in the filament circuit. In securing a given spectrum curve observations were taken at wave-length intervals of about 0.1A. Care was taken to avoid the line spectra of the target. The radiations investigated were those leaving the face of the target at an angle of 45° and making an angle of 90° with the cathode stream.

Reflected intensities were measured by fixing the position of the ionization chamber and rotating the crystal slowly through the proper position for reflection, observing the total ionization occasioned. This method of measurement is fully discussed by Bragg, James, and Bosanquet.[7] Crystal rotation in steps of one minute of arc each second was accomplished by a metronome-controlled electrical device. Results of these measurements are plotted as ordinates in Fig. 1. The tube poten-

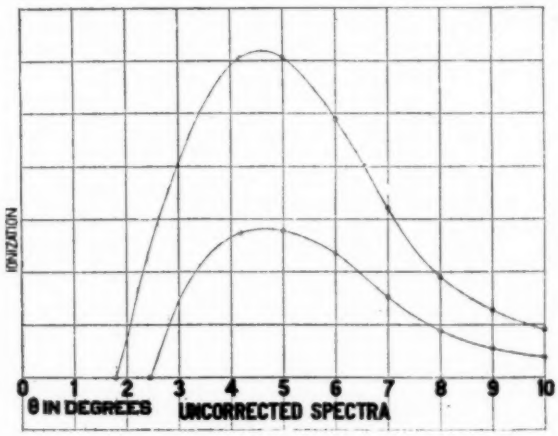

Fig. 1.

tials for the two curves are 70.7 and 51.4 kv. The circles denote observed points with the exception of those on the axis, which were computed from the known tube voltages. The spectrometer slit widths were such that a maximum wave-length range of approximately .05A was to be expected for each angle θ. A crystal rotation of a 1.5° was found sufficient in most cases to cover the full range of reflection.

Order correction. The first correction to be applied to the observed spectra is the elimination of higher order effects. Dauvillier[1] has supposed that the intensities of the several orders simultaneously reflected

[6] Kirkpatrick, Jour. Am. Opt. Soc. etc., Feb. 1923

[7] Bragg, James, and Bosanquet, Phil. Mag. No. 243, p. 309, 1921; No. 247, p. 1, 1921

from a crystal in a common direction are connected through the relation

$$I=\Sigma(I_n/n^3) \qquad (1)$$

I being the combined intensity of reflection and I_n the intensity which a wave-length now reflected in the order n would possess if reflected in the order one. The summation extends over all values of n which may be present in the complex reflection.

The writer has tested this assumption by two experimental methods. The first comprised a study of the type of curve known as the isochromat; a curve giving intensity of x-ray reflection at a fixed angle θ as a function of generating potential. This curve is straight at potentials only slightly greater than that necessary to elicit a reflection and continues straight until twice the starting potential is reached, when the slope of the line abruptly increases; the curve then continues straight until three times the starting potential is attained, when a further, though slight, increase in slope may be observed. Each change in slope results from the entrance

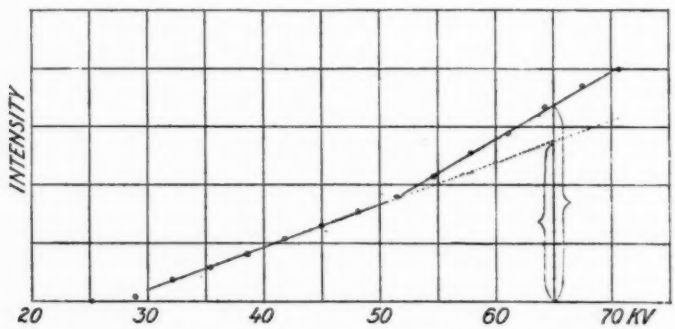

Fig. 2. Dichromat. Variation of intensity of reflection with generating potential.

of a new higher ordered wave-length into the reflection. By extrapolating the portion of the curve due solely to first order intensity, it is at once seen from the graph how the total ionization at any potential is divided between first and higher orders. A large number of curves of this type, which might more properly be called polychromats, were constructed from observed data, and spectra correction factors were computed from them. A sample curve is shown in Fig. 2. The ratio of the ordinates inclosed by the curved brackets gives the fraction of the total reflected intensity which, at 65 kv, is ascribable to first order reflection.

The second method of investigating the strengths of different ordered reflections was the following. The reflected ray under examination, known to contain, say, two orders, was intercepted by a layer of aluminum and the diminution of intensity noted. The absorption coefficients of the two wave-lengths in aluminum were known and hence their

relative strengths in the duplex beam could be computed. Given a beam made up of two wave-lengths having the respective intensities I_1 and I_2, and given K_1 and K_2 as the respective fractions transmitted by a given absorber, then we have the equation $I_1/I_2=(K_3-K_2)/K_1-K_3)$, where K_3 is the observed fraction of the *entire* beam transmitted by the same absorber. The procedure is readily extended to beams of three or more constituent wave-lengths, although beyond three the errors of observation become important, and the accuracy is apt to be low. The following table shows the agreement between this method and the preceding.

Angle θ	*Ratio of first order intensity to total intensity*	
	By absorption	By polychromats
3°	1.00	1.00
4°	.99	1.00
5°	.82	.825
6°	.72	.67
7°*		
8°	.45	.47
9°	.335	.30

*Discarded because of mistakes in absorption measures

By comparison with these results, Eq. (1) appears to be unreliable, ascribing too large a value to the first order in the shorter wave-length region and too small a value (frequently negative) in the longer wave-length region. Furthermore the subtractive nature of the corrections by Eq. (1) makes it particularly unlikely to give an accurate result, for the portion of the total intensity discarded by subtraction at long wave-lengths, is much greater than the portion retained, so that it is easily possible for a 5 per cent error in the estimate of the correction to result in a 50 per cent error in the remaining intensity.

The effect of removal of higher-ordered reflections from the spectra is shown in B of Fig. 3. In this figure A is the upper curve of Fig. 1. A new ordinate scale has been adopted and the abcissae have been changed to denote wave-length instead of crystal angle.

Ionization chamber correction. As a measure of the energy of the reflected rays the amount of ionization resulting from complete absorption in methyl iodide vapor has been taken, with the provision that the K absorption of iodine be excluded from consideration. The reason for this exclusion will soon appear. The ionization chamber used in this work did not actually absorb completely the radiations entering it, but it was possible to determine how far toward completeness the process of absorption went and so to adjust the spectra to the form which complete absorption would have produced. The chamber had an interior length of 41 cm, was closed at the crystal end by an aluminum window .01 cm

thick, and at the other end by a plug of hard rubber. A lead slit limited the entering ray so that within the chamber its minimum distance from the chamber wall was 1.8 cm. The absorption by methyl iodide vapor under the conditions existing in the chamber was determined from spectrometer measurements upon a volume of the vapor contained in a glass cylinder 14 cm long, closed by light cork ends. The absorptions of this cylinder of vapor were determined for five different wave-lengths by the usual method for determining absorption coefficients, and a curve

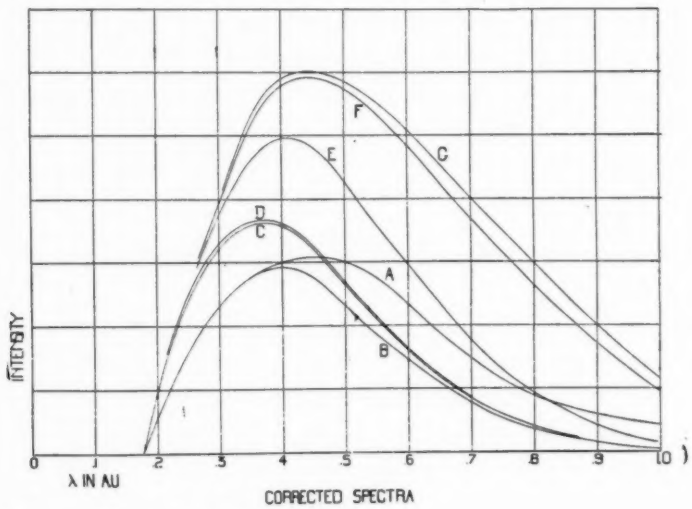

Fig. 3. A. Observed spectrum.
B. Corrected by removal of orders of reflection higher than first.
C. Further corrected for partial absorption by ionization chamber.
D. Further corrected for absorption by chamber window.
E. Further corrected for variation of reflecting power of crystal.
F. Further corrected for absorption by x-ray tube wall.
G. Further corrected for absorption by atmosphere. This curve depicts the (ionizing) energy distribution within the x-ray tube at 70.7 kv.

was plotted from the data, showing the fractions at various wave-lengths which should be absorbed by the ionization chamber of the spectrometer. For all wave-lengths dealt with the absorption by the chamber was above 80 per cent. The correction of the spectra was effected by multiplying each ordinate by the reciprocal of the corresponding fraction absorbed. The effect of this correction is seen in curves B and C of Fig. 3.

Considering now only wave-lengths greater than about .37 A, calculation shows that practically all the energy abstracted from the entering beam within the chamber is actually absorbed by the gas, only a minute portion, of the order of one per cent, reaching the chamber walls. Wave-lengths

shorter than .37 A, however, will excite in the chamber the penetrating K-radiation of iodine, which would dissipate appreciable and unknown amounts of energy in the chamber walls. Furthermore the K discontinuity in the absorption of iodine appears at about the same wave-length, and the absorption data referred to in the preceeding paragraph become inapplicable as they pertain only to the region of L, M, etc. absorptions. For these reasons no spectral energy measurements were made in this short wave-length region, the gap between the observed points and the known quantum wave-length being interpolated.

Window correction. A computation based upon the measured absorption coefficients of aluminum permitted the spectra to be corrected for the small loss at the aluminum chamber window. In Fig. 3 a comparison of

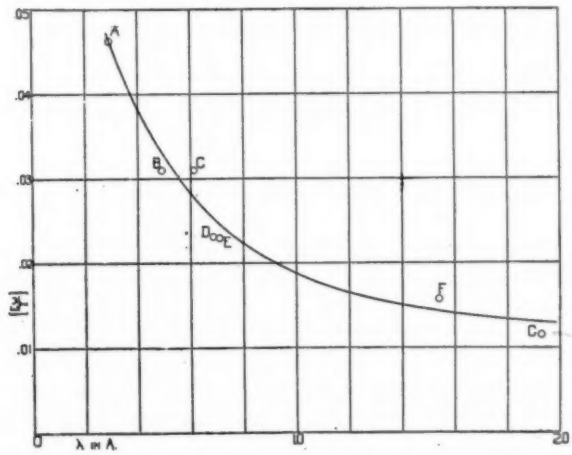

Fig. 4. Points A, B and D by Davis and Stempel;[9] C by Bragg, James, and Bosanquet;[7] E by A. H. Compton;[8] F and G by Wagner and Kulenkampff.[4]

curve C and the corrected curve D shows the effect to be relatively unimportant. The correction has nevertheless been made for all the curves. It is assumed that no important amount of the energy absorbed by the window is re-emitted in any ionizing form within the chamber.

Crystal correction. Bragg and other workers have denoted the reflecting power of crystals by the expression Ew/I where E is the total energy of a given wave-length reflected by the crystal during one sweep through its reflecting position with angular velocity ω, and I is the energy obtainable per second from the same beam before reflection. The absolute

[8] A. H. Compton, Phys. Rev. **10**, 95, (1917)

[9] Davis and Stempel, Phys. Rev. **19**, 504 (1922). The evaluation of $(E\omega/I)$ however does not appear in this reference but was kindly furnished by Professor Davis from an unpublished manuscript.

values of the quantity $E\omega/I$ for seven particular x-ray wave-lengths have been determined by others and are shown in Fig. 4. All pertain to (100) faces of rock salt, prepared, save one, by grinding. ω is in degrees per second.

The curve drawn through these points has been employed for correcting the spectra of this paper. We desire to plot in the corrected spectra the quantity I or at least something proportional to it. From the spectrometric observations we have, or should have if the resolving power of the spectrometer were high, the quantity E. Actually, since the slits are of considerable width and the resulting spectra impure, we have instead $E\,d\lambda$.

Starting with the identity

$$I \equiv \omega \frac{E\,d\lambda}{(E\omega/I)\,d\lambda}$$

and substituting $d\lambda = 2d \cos\theta\, d\theta$, we obtain, k being a constant,

$$I = k\,\frac{(E\,d\lambda)\sec\theta}{(E\omega/I)}$$

which is the quantity desired for plotting. Hence to effect the crystal correction we multiply the ordinates of the given spectrum by the secants of the corresponding angles of reflection and divide by the corresponding coefficients of reflection from Fig. 4. Applying this correction to D of Fig. 3 gives E.

Tube wall correction. Direct measurement of the thickness of the tube wall was attempted by the use of a traveling microscope. The uncertainty in focusing upon the inner surface was considerable and the index of the glass was unknown. The attempt served to show however that the thickness was not the same at all parts of the equator, measurements varying by as much as twenty per cent. For this reason it seems important to make measurements with respect to the particular spot through which the rays to be employed emerge.

The x-ray tube used in the foregoing measurements was removed from its place before the spectrometer and a second tube substituted. The first tube was mounted between the crystal and the ionization chamber of the spectrometer so that it could be readily moved into or out of the path of the reflected ray. This ray in traversing the tube passed along a side of an imaginary equilateral triangle inscribed in the equator of the tube. The tube was turned about its geometrical axis so that one of the points of intersection of the reflected ray with the tube wall fell at that portion of the wall through which rays had been received throughout all the above described work.

The absorptions of the tube for radiations of seven different wave-lengths within the range from .2 to .8A were observed. The resulting values of μx, where x is the glass thickness in the direction of the ray and μ the absorption coefficient, pertain to oblique transmission through two thicknesses of glass wall. They were adjusted so as to apply to single normal transmission through the appropriate spot of the wall by a procedure based upon further absorption measurements with respect to the other two sides of the above mentioned equilateral triangle. The process did not assume uniformity in the thickness of the tube wall. The resulting values of μx when plotted against the 2.8 power of the wave-length fell along an extremely good straight line. The intensity at any wave-length within the tube was readily deduced from these data and a knowledge of the intensities without. See Fig. 3.

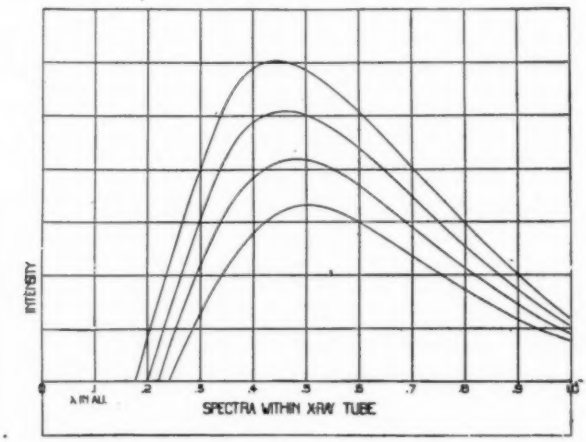

Fig. 5

Air correction. It remains to consider the effects of atmospheric air, which composed 65 cm of the total path length of the radiations. A few direct measurements of the absorption coefficients of air were attempted as well as several computations based upon knowledge of the absorptions of the constituents. In the final corrections, however, Wagner and Kulenkampff's value ($\mu = 3.1 \times 10^{-3} \lambda^{2.8}$) has been followed. The effect of the air correction appears in G of Fig. 3.

Discussion

Curve G in Fig. 3 should show the ionizing energy distribution at the potential 70.7 kv, within the x-ray tube. Fig. 5 repeats curve G, and gives also the corresponding curves at three other potentials. The upper and lower curves of Fig. 5 are the final forms of the spectra of Fig. 1.

The two intermediate curves of Fig. 5 have no independent value as they were not obtained from separate observations. However the observed fact that the isochromats are linear, permits these intermediate spectra to be drawn in with perfect definiteness, that is, with an accuracy as great as that of the observed curves upon which they are based. The rule is that a family of spectrum curves (potential being the parameter and tube current constant throughout) cut off on any ordinate (except quite near the feet of the curves) segments proportional to the differences of their generating potentials. This holds independently of whether the curves have been corrected for absorption, ionization, or reflectivity effects, but requires that the correction for superposition of orders shall have been carried out. Where several members of a family of observed spectrum curves are given, as in the often-cited curves of Ulrey,[10] this rule furnishes an easy means of correcting for the order effects simply from inspection of the graphs. This process is fundamentally the same as the more elaborate procedure applied to the curves of this paper.

As before stated no observations were taken in the region to the left of the 0.4 A ordinate of Fig. 5, so the curvature near the feet of the curves may be slightly other than that shown.

Inspection of the maxima of the curves of Fig. 5 shows that their positions are not in agreement with either the displacement rule of Ulrey or that suggested by Dauvillier. According to the former the product of the wave-length at the maximum by the square root of the generating potential should be constant, while the latter makes the maximum wave-length proportional to the minimum or quantum wave-length. Denoting these wave-lengths by λ_m and λ_o respectively, the present results are found to conform to the relation $\lambda_m = k + k'\lambda_o$, both constants being positive.

It would be very desirable to correct these curves further for absorption of the rays by the target, and so have an expression of the distribution of energy *as emitted*. Knowledge of these effects is not complete enough to allow this. Fortunately the comparison of the present results with theory is not prevented by this limitation, since theories of the continuous spectrum contain their own assumptions about the absorptions of the emerging rays. In Fig. 6 are drawn the proposed energy distributions of three different theorists, all the curves corresponding to voltages near 51 kv and setting forth the distributions within the tube. With them appears the corresponding experimental curve of this work. The forms of these curves only, not the relative heights, are of signifi-

[10] Ulrey, Phys. Rev. **11**, 401 (1918)

cance. The Davis curve results from a new (unpublished) theory of Bergen Davis which considers the radiation to result from the impact of the cathode electrons with the orbital electrons of the target atom. The energy transferred from a cathode electron to an orbital electron is radiated as a single quantum. Behnken[11] gives a distribution equation which includes a term expressing the absorptions of the tube wall. Neglecting this term we may write as Behnken's distribution within the tube;

$$I=\frac{1}{\lambda^{2.8}}\left[1-e^{-3.6(\nu_0-\nu)/\nu^{2.8}}\right]$$

This equation is plotted in Fig. 6. The March curve is plotted from the equation

$$I=\lambda^{-4.5}e^{-4.5\lambda_m/\lambda}$$

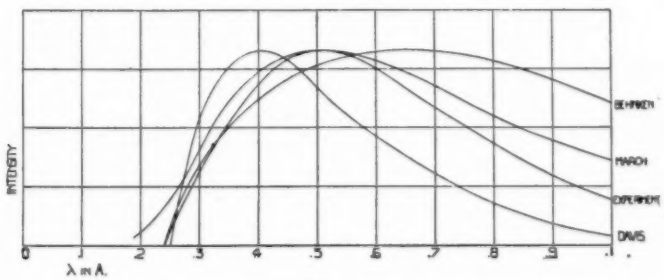

Fig. 6

The discrepancies between the theoretical and experimental curves are wide. Probably no real agreement is to be expected until more knowledge is obtained relative to the penetration of cathode electrons and the wave-length variation of the mechanical equivalent of ionization.

The writer desires in conclusion to express his thanks to Professor Elmer Dershem of the University of California for advice and help throughout this work and to record his appreciation to Professor Bergen Davis of Columbia University for his interest and for the data supplied.

PHYSICAL LABORATORY,
UNIVERSITY OF CALIFORNIA,
January 17, 1923

[11] Behnken, Zeit. für Phys. **4**. 241, 1921

A SPECTROGRAPHIC STUDY OF ULTRA-VIOLET FLUORESCENCE EXCITED BY X-RAYS

By J. O. Perrine

Abstract

Fluorescent spectra excited by x-rays.—(1) *Ultra-violet.* In order to photograph the spectrum, the specimen being studied was placed in front of the slit of a Fuess single-prism quartz spectrograph and was exposed to x-rays from a Coolidge tube with the target about 12 cm off. With the tube operating at .002 amp. and 50 kv and a slit width of .15 mm, exposures up to 15 hours were made. *Over one hundred substances* were tested. Fourteen double salts of uranium, 23 oxides, 50 other compounds and also anthracene, chrysoidine, eosin and fluorescine gave no ultra-violet fluorescence, though some show brilliant bands in the visible; but positive results were obtained with *the chlorides of Cd, Cs, Li, K, Na, and Rb, and also with KBr, KI, $BaSO_4$, $RaSO_4$ and $CaWO_4$.* NaCl gave a strong band with maximum at 2470A and CsCl gave a band extending from 5720 to 2340A with three maxima. Several willemite screens, some x-ray intensifying screens and one fluoroscopic screen also showed ultra-violet fluorescence. The intensity of fluorescent response decreased for successive exposures. (2) *Visible fluorescence.* One or more bands in the visible were emitted by all the salts showing ultra-violet fluorescence, except barium and radium sulfates, and also by ZnO, CdI, Cu_2I_2 and HgCl and, of course, by the uranyl salts.

Changes of color of chlorides due to x-rays.—RbCl was observed to turn dark blue, NaCl buff, KCl and LiCl pink, and CsCl blue. The original white color was restored by exposure to sunlight, but did not return in the dark. This change may be due to a reduction to the metal and Cl, which is then occluded. The salts had been carefully purified.

Photo-electric photometer for measuring distribution of density in a spectrogram is described. A Kunz cell was used.

IF x-radiation, which is of the order of one angstrom in wave-length is used as the incident radiation, one would expect in accordance with Stokes' law that, in addition to the fluorescent radiation produced in the visible region, fluorescence in the ultra-violet region might be produced.

The first study of the production of ultra-violet fluorescence by x-rays was made by Winkelman and Straubel.[1] In the case of fluorspar, they report a band of fluorescent radiation extending from 3,960A to 2,330A with a maximum of 2,800A. Schuhknecht[2] examined spectrographically

[1] Winkelman and Straubel, Wied. Ann. 1896

[2] Schuhknecht, Ann. der Phys. **17**

the fluorescence emitted from a number of natural minerals and inorganic compounds under x-ray excitation. The following substances are reported by him to give fluorescent radiation of wave-length less than 4000A; fluorspar, two samples; uranium ammonium fluoride, and scheelit.

The fluorescent materials used in x-ray fluoroscopic and intensifying screens were studied by Hodgson.[3] When excited by x-rays, these substances gave evidence of fluorescence in the ultra-violet. According to his work, the fluorescent radiation from calcium tungstate extends to approximately 3650A.

Apparatus and Experimental Procedure

The substance under examination was placed in front of the slit of a Fuess spectrograph[4] with the surface of the specimen at an angle of 45°

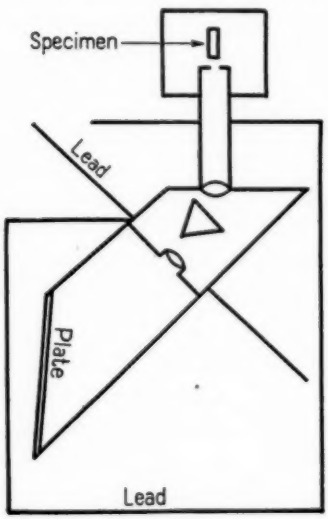

Fig. 1. Optical system.

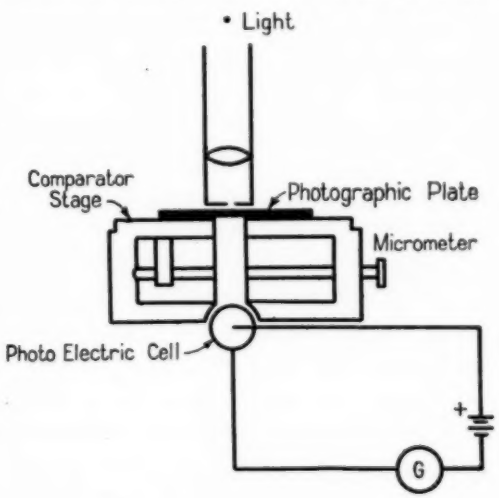

Fig. 2. Photo-electric spectro-photometer.

with the vertical face of the collimator head. The x-ray tube was placed directly above the specimen so that the x-rays passed through the top of a light-tight box fastened to the end of the collimator. By this arrangement all extraneous light was excluded. The distance from the specimen to the x-ray target was approximately 12 cm.

Fig. 1 shows the general arrangement of the optical system. The plate holder could be moved in a plane perpendicular to that of the figure, and exposure could thus be obtained at various places on the same photographic plate. A Stanley plate, 6 by 9 cm, was used.

[3] Hodgson, Phys. Rev. **12**, 431 (1918)

[4] Zeit. für Instrumentenkunde **28**, 34. Instrument used is referred to as No. 3

A quartz mercury arc lamp was used to obtain a calibration spectrum on the photographic plate directly above and below the fluorescent spectrum. The intensity of the fluorescent radiation was so small that an exposure of several hours was necessary even though a slit width of .15 mm was used.

As a source of x-rays, a radiator type Coolidge tube was used with a current of two or three milliamperes at 50,000 volts.

In taking photographs under the conditions described, it was found that diffusely scattered x-rays caused the plate to be badly fogged even though the x-ray tube was provided with the usual lead glass shell directly about the bulb. Protection from these scattered x-rays was secured by lead screens made of two layers of 1/16-inch thick lead. In some plates, a shadowgraph of a small metal clip on the rear side of the plate holder was obtained. This particular circumstance together with the general fogging indicated very definitely that diffuse x-radiation came from the brick wall situated about three feet away from the rear side of the spectrograph and the x-ray tube. It was found necessary to surround the spectrograph completely by these lead plates, and in the final arrangement, satisfactorily clear negatives were obtained even after exposures of fifteen hours.

Photo-electric photometer for measuring the blackening of the photographic plate. Fig. 2 shows the general arrangement of the apparatus. The eye piece, cross hair and objective of the comparator telescope were removed, leaving only the telescope tube. A 100-watt, single coil filament lamp was mounted on the telescope tube at the upper end. A lens placed within the base of the tube focused the light from the lamp on a slit at the center of a metal plate fitted in the lower end of the tube. The slit was .25mm wide and 2mm high and was usually lowered to within .5mm of the surface of the plate, which was placed on the comparator stage. The light which was transmitted by the small area of the plate in front of the slit, entered the photo-electric cell. Proper precautions were taken to keep out all extraneous light.

The Elster and Geitel type of photo-electric cell was first tried, but the leakage current, or so-called dark current observed was so large that reliable results could not be obtained. The Kunz[5] photo-electric cell was, however, found to be very satisfactory. When 120 volts were used, the dark current seldom exceeded 2 per cent of the maximum light current, and after the circuit had been closed for 15 minutes it decreased to .5 per cent of the maximum light current. Within the light-tight box containing the photo-electric cell a beaker of concentrated sulphuric acid

[5] Kunz and Stebbins, Phys. Rev. **7**, 282 (1916)

was placed to assist in decreasing the leakage over the surface of the cell.

A Leeds and Northrup type "C" galvanometer (sensibility 11900 megohms) was used, and the entire arrangement was so sensitive that the 100-watt lamp could be operated at 15 per cent below normal rating, and only 55 volts need be applied to the photo-electric cell. The incandescent lamp and the photo-electric cell were operated by separate

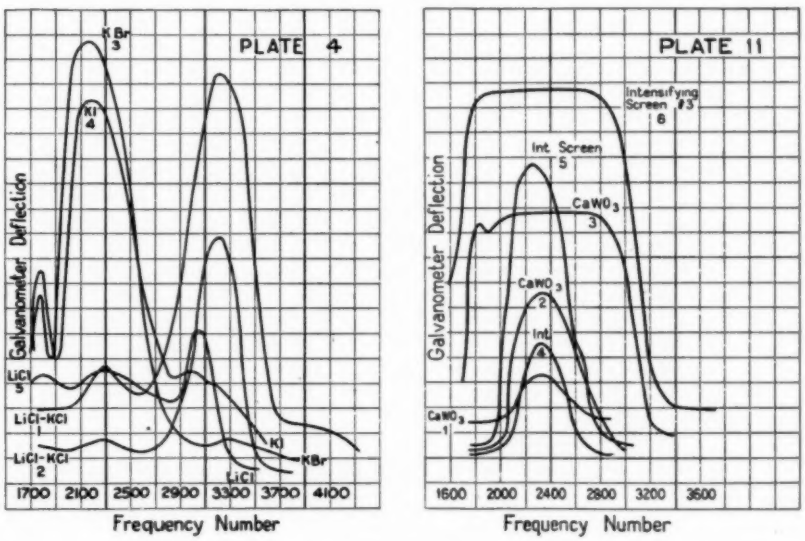

Fig. 3. Blackening distribution curves.

PLATE 4

Curve 1. Recrystallized mixture LiCl-KCl—10 hours' exposure
Curve 2. Recrystallized mixture LiCl-KCl— 4 hours' exposure
Curve 3. Potassium bromide — 4 hours' exposure
Curve 4. Potassium iodide —14 hours' exposure
Curve 5. Lithium chloride — 6 hours' exposure

PLATE 11

Curve 1. Calcium tungstate — 1-min. exposure
Curve 2. Calcium tungstate — 2-min. exposure
Curve 3. Calcium tungstate —30-min. exposure
Curve 4. Intensifying screen #3— 1-min. exposure
Curve 5. Intensifying screen #3— 2-min. exposure
Curve 6. Intensifying screen #3—30-min. exposure

storage batteries. Observations showed that a change in the potential used in the photo-electric cell circuit did not change the relative value of reading throughout some particular fluorescent band.

FLUORESCENT SPECTRA

The experimental results are given in Figs. 3–6 and in Tables I and II. In the blackening distribution curves, galvanometer deflections are

used as ordinates, and are referred to the upper left-hand corner of the page as the origin of axes. Frequency numbers, i.e., the reciprocals of wave-length in centimeters, are used as abscissae.

Change of Intensity of Fluorescence Under Continued Action of X-Rays

In the early part of the work, several samples of willemite, which gave positive results, were subjected to repeated exposures for checking pur-

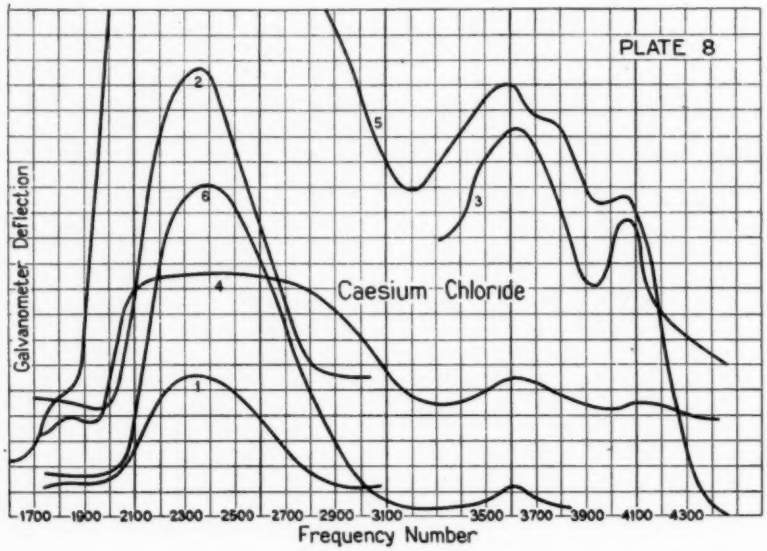

Fig. 4. Plate 8

Curve 1. 6-minute exposure
Curve 2. 20-minute exposure
Curve 3. 5-hour exposure with microphotometer at high sensibility to bring out second and third bands
Curve 4. 3.5-hour exposure with microphotometer at low sensibility
Curve 5. 5-hour exposure with microphotometer at high sensibility
Curve 6. 30-minute exposure to bring out second band faintly

poses. These samples gave fluorescence of decreasing intensity under these repeated exposures. Two samples, particularly, which had given fine blackening of the plate at a region corresponding to 3560A, later gave very faint blackening in this region. Other conditions were thought to be the same, in fact, the intensity of the x-radiation was greater in the later tests than in the former ones. These two samples were again exposed after two months' time. They failed to show any recovery during this interval.

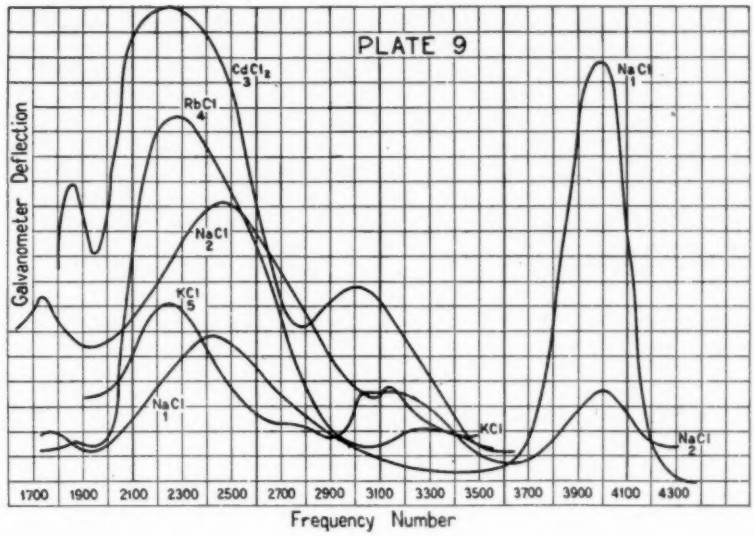

Fig. 5. PLATE 9

Curve 1. Sodium chloride —15-hour exposure—Sample #1
Curve 2. Sodium chloride — 8-hour exposure—Sample #2
Curve 3. Cadmium chloride — 5-hour exposure
Curve 4. Rubidium chloride—12-hour exposure
Curve 5. Potassium chloride— 8-hour exposure

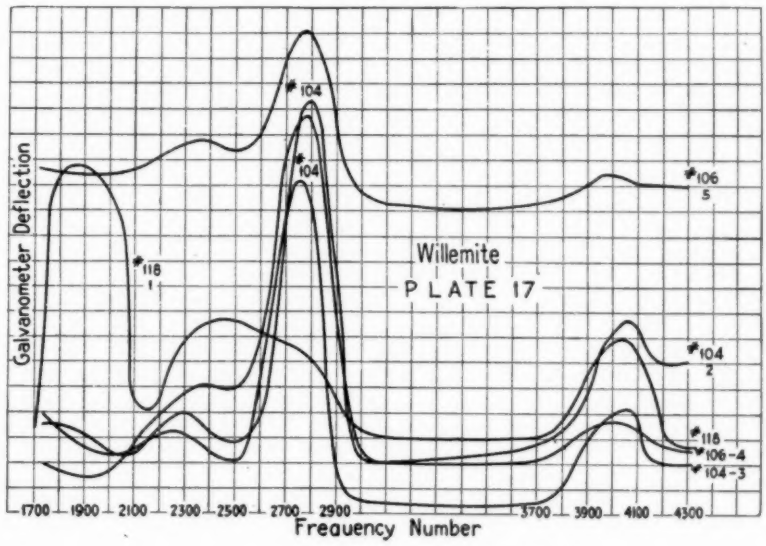

Fig. 6. PLATE 17. Willemite

Curve 1. Number 118—7.5-hour exposure
Curve 2. Number 104— 7-hour exposure—Sample #1
Curve 3. Number 104— 7-hour exposure—Sample #2
Curve 4. Number 106— 11-hour exposure—Sample #1
Curve 5. Number 106— 11-hour exposure—Sample #2

TABLE I. COMPOUNDS SHOWING NO ULTRAVIOLET FLUORESCENCE

The number following each salt indicates the number of hours exposure to x-rays.

Uranyl Compounds

Ammonium potassium uranyl chloride (5)
*Barium uranyl acetate (12)
*Caesium uranyl chloride (12)
*Cadmium uranyl acetate (8)
*Lead uranyl acetate (12)
*Lithium uranyl acetate (10)
*Mercuric uranyl nitrate (8)
*Potassium uranyl acetate (3)
*Rubidium uranyl nitrate (5)
*Rubidium uranyl sulfate (5)
*Silver uranyl nitrate (13)
Strontium uranyl acetate (2)
Thallous uranyl sulfate (8)
Uranyl tellurate (13)

Oxides

Aluminum oxide (5)
Antimony oxide (12)
Barium oxide (10)
Bismuth oxide (10)
Berylium oxide (6)
Cadmium oxide (6)
Calcium oxide (12)
Calcium peroxide (5)
Cuprous oxide (5)
Cupric oxide (5)
Erbium oxide (10)
Germanium oxide (5)
Magnesium oxide (8)
Magnesium peroxide (5)
Silicon oxide (12)
Silicon dioxide (10)
Strontium oxide (6)
Strontium peroxide (5)
Tin oxide (12)
Uranium oxide (15)
Uranium peroxide (18)
*Zinc oxide (8)
Zinc peroxide (8)

Miscellaneous Compounds

Anthracene (5)
Barium chloride (5)
Berylium chloride (5)
Cadmium bromide (5)
Cadmium fluoride (5)
[1]Cadmium phosphate (5)
[1]Cadmium sulfide (5)
Caesium aluminum sulfate (5)
Caesium di-chor-iodide (5)
Calcium Sulfide (10)
Chrysoidine (5)
Copper selenate
Cupric bromide (7)
Cupric sulfide (5)
Didymium chloride (7)
Eosin (crystal) (5)
Fluorescine (5)
Indium iodate (5)
[3]Iron pyrites (5)
Magnesium perborate (4)
Mercuric chloride (5)
Mercuric copper iodide (7)
Mercuric iodide (7)
Mercuric sulfide (5)
Molybdenic acid (5)
[3]Molybdenite (6)
Potassium auri bromide (5)
Potassium cuprisulfide (7)
Potassium fluoride (4)
Potassium fluotitanate (5)
Potassium periodate (7)
Rochelle salts (5)
Rubidium di-chor-iodide (5)
[2]Silver bromide (5)
[2]Silver chloride (5)
Silver dichromate (5)
[2]Silver iodide (5)
Silver mercuric iodide (7)
Sodium boro-fluorate (5)
Sodium fluoride (5)
Sodium periodate (5)
Sodium silicate (5)
[3]Stibnite (5)
Strontium chloride (5)
Sulfur (block) (10)
Telluric acid (5)
Thallium bromide (5)
Thallium chloride (5)
Thorium nitrate (5)
Tin chloride (5)
Tungstic acid (5)
Zinc (sheet) (5)
Zinc bromide (4)
[1]Zinc sulfide (12)

*Give narrow fluorescent bands in the visible.

[1] Reported by Dr C. W. Waggoner as highly purified and not fluorescent under excitation by ultra-violet light.

[2] These three silver salts had been freshly prepared and kept from ordinary light at all times.

[3] These three sulfides were large crystals with flat mirror-like surfaces.

TABLE II. COMPOUNDS WHICH GAVE POSITIVE RESULTS

Substance	Frequency number limits of band	Frequency number of maximum	Time of exposure to x-rays
Barium sulfate	2000–3700	2610	6 hours
Barium sulfate Radium sulfate	2100–3200	2750	12
Cadmium chloride		See Plate 9, Fig. 5	
Cadmium iodide	1700–1950 2000–2400	1810 2190	5
Caesium chloride		See Plate 8, Fig. 4	
Calcium tungstate		See Plate 11, Fig. 3	
Cuprous iodide	2100–2450	2300	10
Lithium potassium chloride (Chemical Dept. sample)	2800–2880 2880–3600	2840 3220	12
Lithium potassium chloride (50–50 mechanical mixture)	2000–2600 3000–3600	2220 3220	4
Lithium potassium chloride (50–50 recrystallized mixture)		See Plate 4, Fig. 3	
Lithium chloride		See Plate 4, Fig. 3	
Mercurous chloride	1750–1850	1800	5
Potassium bromide		See Plate 4, Fig. 3	
Potassium iodide		See Plate 4, Fig. 3	
Potassium chloride		See Plate 9, Fig. 5	
Rubidium chloride		See Plate 9, Fig. 5	
Sodium chloride		See Plate 9, Fig. 5	
Willemite 104		See Plate 17, Fig. 6	
Willemite 118		See Plate 17, Fig. 6	
Willemite 106		See Plate 17, Fig. 6	
X-ray intensifying screen No. 3 (Patterson)		See Plate 11, Fig. 3	
X-ray fluoroscopic screen No. 1 (Patterson)	1600–2780 1700–1900 1900–2600 1800–2500	Flat 1800–2320 1810 2190 2210	5.5
Zinc oxide	1700–1850 1950–2300	1775 2070	5

In the case of all the samples of artificial willemite which gave positive results, three fluorescent bands were present. In some samples the band in the visible was very faint, while in other samples the two ultra-violet bands were very faint. In all cases where the far ultra-violet band was strong enough to permit of measurement, the maximum blackening of the plate checked at a frequency number of 4050. All of the samples of artificial willemite had been made by Mr D. T. Wilber of the Physics Department, Cornell University.

In considering these curves, it will be noticed that the points of maxima for potassium iodide and potassium bromide are almost exactly at the same frequency number. However, cuprous iodide has a maximum at 2300, which is the same as one of the maxima for potassium bromide and iodide. Potassium chloride has a maximum at 2250, while lithium

chloride has a maximum at 2290. Caesium chloride has one of its maxima at 2340. Sodium chloride and caesium chloride each has a band at a point located at about 4000. Caesium chloride gave most beautiful photographic records of ultra-violet fluorescence. The two maxima in the ultra-violet are very readily seen by visual inspection of the original negative. The fluorescence extends very definitely out to 2250 A.

Change in Color Due to Exposure to X-rays

In connection with these experiments, some marked color changes were observed. Highly purified rubidium chloride, which is a white salt, became a dark blue, looking very much like a piece of copper sulphate. This color change was observed after an exposure of five hours. The photographic plate gave evidence of both visible and ultra-violet fluorescence. It was then a question whether or not this specimen already a dark blue, would fluoresce upon further excitation by x-rays. It was found to fluoresce as strongly as before. Upon removing the specimen and exposing it to ordinary day-light, the original whiteness returned within three hours.

A sample of highly purified sodium chloride turned to a marked buff color. The original whiteness of the salt was not restored in three days. Potassium chloride and lithium chloride became pink under the action of x-rays. In these two cases the original color returned within an hour. Potassium bromide took on a light blue and potassium iodide a brown-buff color. Caesium chloride turned to a dark blue and returned within an hour. As in the case of rubidium chloride, caesium chloride, which had been turned blue by exposure to x-rays, was tested again and fluoresced equally well during the second exposure. To determine whether there might be some fluorescent radiation emitted during the time in which the original white color was returning, the substance was left in the light-tight box, the photographic plate moved to a different exposure surface and a 36-hour exposure taken. At the end of this time, the specimen was still as blue as at the beginning and no evidence of fluorescence appeared on the plate. It was found on exposure to daylight that the substance turned white within five minutes.

It is not unlikely that these color changes were due to a reduction of a small fraction of the chloride into the metal concerned and free chlorine. The chlorine, perhaps, is retained by adsorption in the unreduced portions. The entire mass appeared to be changed in color but it is very possible that the reduction of a small amount is sufficient to give color to the entire mass. Exposure to light appears to be necessary in order to

reverse the change. The fact that a specimen exposed once gave further fluorescence on a second exposure, would not necessarily indicate that the fluorescence did not accompany the color change. As stated above, a small amount of reduced salt might color the entire mass so that during the exposure the continual reduction might occur with resulting fluorescence. To the eye, however, no additional color changes took place.

Whenever the specimen, after an exposure, showed a color change the developed plate gave evidence of ultra-violet fluorescence except for silver bromide, silver iodide and silver chloride. The color changes in these three salts were much less than had been expected since they show marked color changes when exposed to ordinary daylight.

The rubidium, potassium, and sodium chlorides had been carefully prepared[6] and were highly purified as far as the presence of other metals was concerned. Spectroscopic examination confirmed the absence of calcium and magnesium.

In conclusion, the writer wishes to express his appreciation for the kindly interest and encouragement of Professor Ernest Merritt under whose direction the work was done. For advice and suggestions given by other members of the Department of Physics, the writer is also indebted.

CORNELL UNIVERSITY,
January 9, 1923

[6] The actual preparation was made by Dr Papish of the Chemistry Department, Cornell University.

EFFECT OF TENSION ON CHANGE OF RESISTANCE AND THERMOELECTROMOTIVE FORCE BY TRANSVERSE MAGNETIZATION

By Alpheus W. Smith

Abstract

Effect on the resistance and thermoelectromotive force of nickel wires, of tension combined with transverse magnetization.—The wires 10 cm long and .14 cm in diameter were stretched while being magnetized transversely with a field of from 1000 to 9000 gauss. The application of tension was found to cause a marked decrease in the change due to the transverse magnetic field, both $\Delta R/R$ and $\Delta E/E\Delta t$ being decreased to half or less by a stress of 20 kg/mm^2.

Effect on the Hall and Nernst effects in a nickel plate, of tension in the direction of the electric and thermal currents was studied for a tension of 28.5kg/mm^2 and for fields up to 20,000 gauss and found to be zero. These results suggest that the Hall and Nernst effects are associated with the action of the magnetic field not on the atoms but on the free electrons, while the change of resistance and of thermoelectromotive force in a magnetic field are associated with a deformation of the atoms by the field.

Ewing's model of the ferromagnetic atom in which elliptic electronic orbits supply the magnetic control and a circular orbit the necessary Weber elements, is shown to account for the changes of length, of resistance, and of thermoelectromotive force on magnetization and the effect of tension on these changes if we assume the nickel atom is compressed in the direction of magnetization and expands at right angles, and that tension increases the stability of Weber elements with planes in the direction of the magnetic field.

IN an earlier paper the author[1] considered the influence of tension on the change of length, resistance, and thermoelectromotive force in a longitudinal magnetic field for a number of ferromagnetic substances. In nickel there was found a marked parallelism between the effects of tension on the changes of thermoelectromotive force, length, and resistance. In view of this fact it seemed of interest to study these changes in a transverse magnetic field. Because of a possible relation between the changes of resistance and the change of thermoelectromotive force on the one hand and the Hall effect and the Nernst effect on the other hand, some observations were made on the effect of tension on the Hall effect and the Nernst effect. Tomlinson[2] has pointed out that the influence of stress on

[1] Smith, Phys. Rev. **19**, 285, 1922

[2] Tomlinson, Trans. Roy. Soc. **174**, 1–173, 1883

the Hall effect might give information concerning the nature of this effect.

Methods of Observation

The specimens to be studied were in the form of thin wires 10 cm long and 1.4 mm in diameter. These wires were suspended between the poles of a large electromagnet, with rectangular faces 9.5x1.8 cm, so that the magnetic field was perpendicular to the axis of the wire. For the measurement of the change of resistance suitable lead wires were soldered to the specimens so that the specimens could be connected to one side of a Kelvin double bridge by which the change of resistance was measured in the way described in a former paper.[1] The tensions were applied by placing different weights in a scale pan suspended from the wire. The observations were made at room temperature.

The change in the thermoelectromotive force was measured on a White double potentiometer. The method of observation was the same as that used in the study of the change of thermoelectromotive force in a longitudinal magnetic field. One junction was in steam at atmospheric pressure. The other was in water at room temperature. All possible precautions were taken to secure a constant difference of temperature between the junctions during a series of observations.

The Hall effect and the Nernst effect were measured by the methods employed by the author in previous studies of these effects.[3] The observations on the Hall effect were made at room temperature. The thermal flow necessary for producing the Nernst effect was obtained by keeping one end of the nickel plate on which the observations were being made at the temperature of steam at atmospheric pressure and the other end at a temperature of about 22°C. It was necessary to make provision for the application of tension to the plate. In the case of the Hall effect this tension was in the direction of the primary current. In the case of the Nernst effect the tension was applied in the direction of the thermal flow. To secure the necessary tensions, the plates were suspended between the poles of the electromagnet and weights hung from the end of a lever which was supported by one end of the plate. In this way an amplification of the applied force was obtained.

Experimental Results

Fig. 1 shows the results obtained from the observations on the change of resistance in electrolytic nickel in a transverse magnetic field. The

[3] Smith, Phys. Rev. **30**, 1, 1910; **32**, 193, 1911

magnetic fields have been plotted as abscissae and the fractional change of resistance as ordinates. The change of resistance in this instance is a decrease. The tensions given on the curves have been expressed in kilograms per mm². The application of tension decreases the change of resistance produced by the transverse magnetic field, a tension of 26.2 kg per mm² causing the change of resistance to decrease to less than one fourth its value for the wire without tension, whereas in the case of a

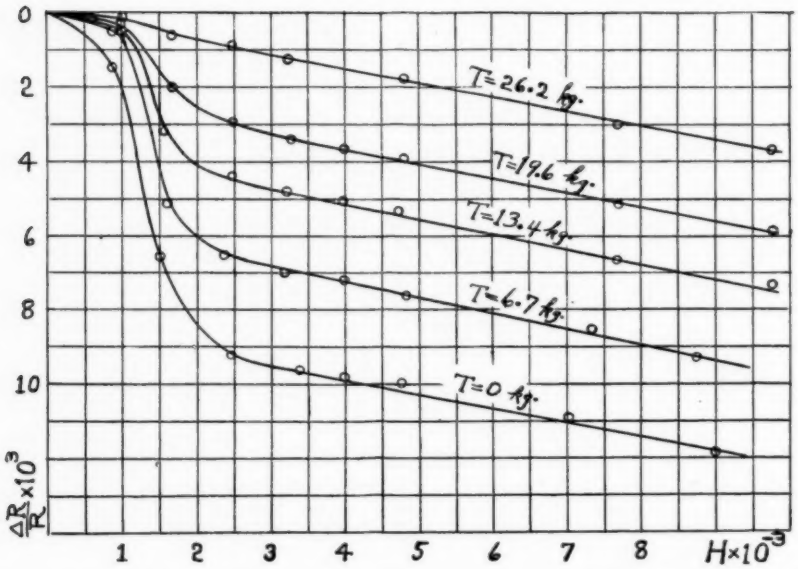

Fig. 1. The Effect of Tension on the Transverse Change of Resistance in Nickel.

longitudinal magnetic field the application of tension lessened the increase of resistance produced by smaller magnetic fields and increased the change produced by the higher magnetic fields.

In Fig. 2 the change of thermoelectromotive force in nickel against copper in a transverse magnetic field has been plotted against the magnetic field producing the change. The fractional changes in the thermoelectromotive force per degree difference in temperature between the junctions have been used as ordinates. This is the mean change for the couple when one junction is at 100°C and the other is at a temperature of about 22°C. The transverse magnetic field produces an increase in the thermoelectromitive force of the nickel against copper as shown in the figure. The application of tension operates to decrease the change of thermoelectromotive force produced by the transverse magnetic field whatever the intensity of the field, whereas in the case of a longitudinal

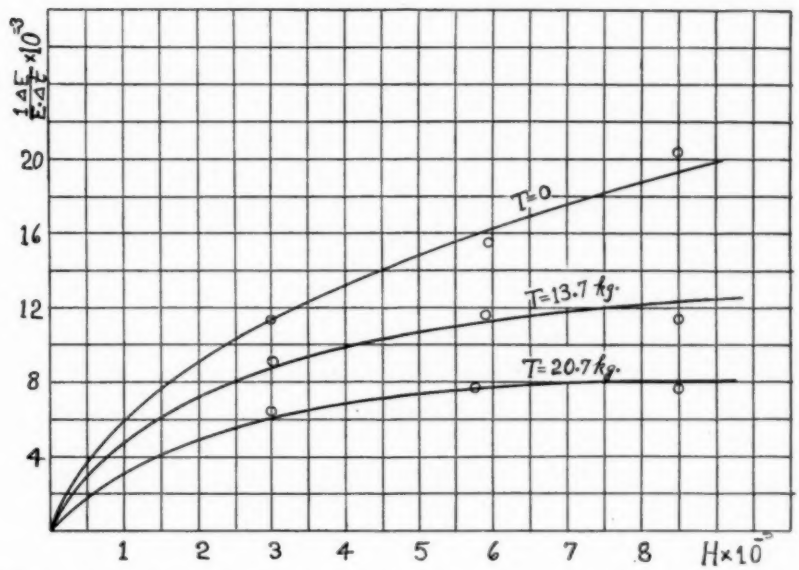

Fig. 2. The Effect of Tension on the Transverse Change of Thermoelectromotive Force in Nickel.

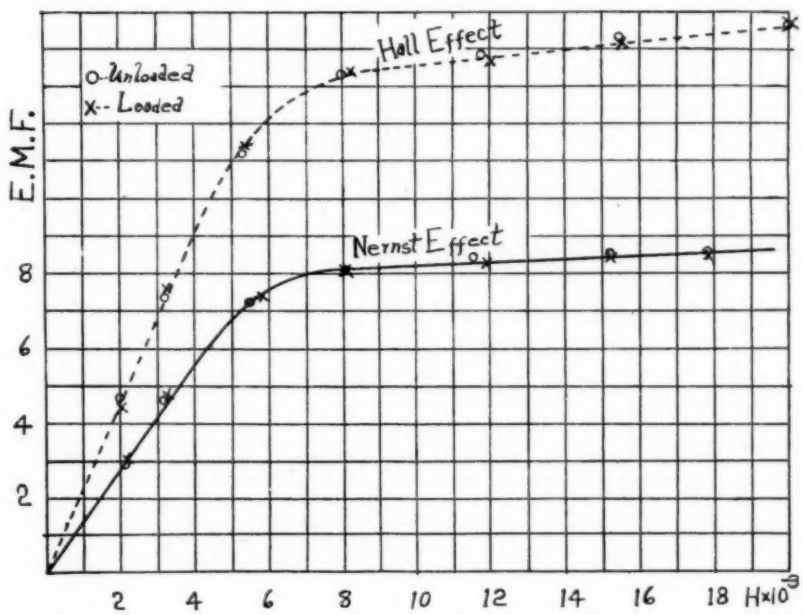

Fig. 3. The Hall Effect and the Nernst Effect in Stressed and Unstressed Nickel.

magnetic field it decreases the change of thermoelectromotive force for lower magnetic fields but increases this change for higher magnetic fields.

In Fig. 3 the dotted curve shows the Hall electromotive force in arbitrary units as a function of the magnetic field. The continuous curve shows the Nernst electromotive force as a function of the magnetic field. The circles on these curves are points obtained when the plate was unloaded. The points marked by crosses were obtained when there was a tension of 28.5 kg per mm^2 in the direction of the electric or thermal current. From these two curves it is seen that neither the Hall effect nor the Nernst effect is appreciably influenced by tension.

This negative result differs from the positive results found for the effect of tension on the change of resistance and thermoelectromotive force in a transverse magnetic field, although in each of these cases, the magnetic field is perpendicular to the direction of the tension and the tension is in the direction of the electric or thermal current. Yet tension has a marked influence on the transverse change of resistance and on the change of thermoelectromotive force but no appreciable influence on either the Hall effect or the Nernst effect.

Discussion of Results

According to Ewing's[4] recent model there is inside of a ferromagnetic atom a Weber element possessing magnetic moment and capable of being turned into allignment by sufficiently strong magnetic forces. In the case of the Bohr type of atom the necessary magnetic control is supplied by the electrodynamic action of the elliptic electronic orbits with a common focus at the nucleus of the atom. A circular electronic orbit with its center also at the common focus of the elliptic orbits supplies the necessary Weber elements. The planes of the elliptic orbits are fixed while that of the Weber element can turn. Ewing suggests that such an atom may be deformed by the application of stresses. It seems quite reasonable to suppose that it may also be deformed during the process of magnetization, on account of changes in the magnitudes of the electrodynamic forces between the Weber element and the fixed elliptic electronic orbits. It is of interest to see what this model of the ferromagnetic atom suggests as an explanation of the changes of length, resistance, and thermoelectromotive force which are observed in nickel in a longitudinal and in a transverse magnetic field.

Suppose that when the nickel atom is brought into a longitudinal magnetic field and the Weber element is oriented with its plane per-

[4] Ewing, Phil. Mag. (6) **43**, 493, 1922

pendicular to the magnetic field, the electrodynamic action between the Weber element and the fixed electronic orbits is such as to produce a contraction of the atom in the direction of the magnetic field and an expansion in the direction perpendicular to the magnetic field. This contraction of the atom in the direction of the magnetic field would, in agreement with the observations, produce a decrease in the length of the metal. The elongation in the direction perpendicular to the magnetic field would, on the other hand, produce the elongation observed in that case. By assuming that the atoms of nickel are oblate spheroids which can be oriented by the magnetic field, Williams[5] explains in much the same way these changes in length. It seems more reasonable to suppose that the flattening of the atom is produced by the magnetic field. Besides it is doubtful as Ewing points out, whether the atom as a whole is oriented by the action of the magnetic field.

If tension in the direction of the magnetic field increases the stability of the Weber elements with planes coinciding with the direction of the magnetic field and decreases the stability of those with planes perpendicular to this direction, fewer Weber elements will be turned with their planes perpendicular to the magnetic field than would be turned by the same magnetic field in a wire without tension. Hence the contraction in the direction of the magnetic field will be less than it would be without the tension and the expansion at right angles to the magnetic field will also be decreased. Honda and Terada[6] find that the application of tension in the direction of the magnetic field decreases the change of length produced by the magnetic field until saturation is nearly reached, where the reverse takes place. There seem to be no observations on the effect of tension on the change of length in a transverse magnetic field.

Suppose that in nickel the greater part of the electric current is carried by electrons which pass from atom to atom or from atom to metal ion when conducting contact is made as a result of the incessant collisions between atoms and atoms or between atoms and ions.

Let σ = electrical conductivity of this kind; n = number of free electrons participating in the transfer of the electric current; l = the effective mean free path of electrons passing from atom to atom or from atom to ion; m = mass of electron; e = the electronic charge; v = mean velocity of electrons; T = tension applied to the wire; and H = the intensity of the magnetic field.

Then $$\sigma = \frac{2e^2nl}{mv} \text{ and } \left(\frac{\delta\sigma}{\delta T}\right) = \frac{2e^2n}{m}\left(\frac{\delta l}{\delta T}\right).$$

[5] Williams, Phys. Rev. **1**, 257, 1913

[6] Honda and Terada, Phil. Mag. (6) **13**, 36, 1907

If the nickel atom is elongated by tension,

$$(\delta l/\delta T)>0 \quad \text{and} \quad (\delta\sigma/\delta T)>0.$$

This is in agreement with the observations of Tomlison[2] and Bridgman[7] who find that the application of tension increases the conductivity of nickel.

Since according to this view the atom contracts in the direction of the magnetic field, the effect of a longitudinal magnetic field on the resistance of nickel is determined by the changes in the dimensions of the atom in the direction of the electric current.

$$\left(\frac{\delta\sigma}{\delta H}\right)=\frac{2e^2n}{mv}\left(\frac{\delta l}{\delta H}\right).$$

Since when the magnetic field is in the direction of the current, $(\delta l/\delta H)<0$, it follows that $(\delta\sigma/\delta H)<0$.

If the magnetic field is perpendicular to the direction of the current, $(\delta l/\delta H)>0$ and $(\delta\sigma/\delta H)>0$. These results are in agreement with the observations that the resistance of nickel increases in a longitudinal magnetic field but decreases in a transverse magnetic field.

Under the simultaneous action of tension and the magnetic field,

$$\frac{\delta}{\delta T}\left(\frac{\delta\sigma}{\delta H}\right)=\frac{2e^2n}{mv}\frac{\delta}{\delta T}\left(\frac{\delta l}{\delta H}\right).$$

Since $(2\ e^2n/mv)$ is inherently positive,

$$\frac{\delta}{\delta T}\left(\frac{\delta\sigma}{\delta H}\right) \text{ and } \frac{\delta}{\delta T}\left(\frac{\delta l}{\delta H}\right)$$

must always have the same sign. Now in nickel a decrease in length due to a longitudinal magnetic field is accompanied by a decrease in electrical conductivity. Hence if the application of tension decreases the change of length produced by the longitudinal magnetic field, it will also decrease the change of electrical conductivity produced by this field. This parallelism between the effect of tension on the change of resistance and the change of length in a longitudinal magnetic field has already been pointed out.

When the magnetic field is perpendicular to the direction of the current and the tension, $(\delta\sigma/\delta H)>0$ and $(\delta l/\delta H)>0$. Hence the application of tension should decrease the change of electrical conductivity produced by a transverse magnetic field, when it decreases the change of length produced by such a transverse magnetic field. The observations described in this paper show that the effect of tension is to decrease the transverse change of resistance but there seem to be no observations

[7] Bridgman, Am. Acad. Arts and Sci. **57**, 41, 1922

on the effect of tension on the change of length in a transverse magnetic field with which to compare these results.

If the deformation of the atom produced either by the magnetic field or by tension is a function of the temperature, there will be a change in the equilibrium between the electrons and the atoms at the ends of an unequally heated wire. This change of equilibrium will manifest itself as a thermoelectromotive force which may be taken as proportional to the intensity of magnetization. Whatever, then, influences the intensity of magnetization will influence the thermoelectromotive force in much the same way and there follows the observed parallelism between the effects of tension on the change of thermoelectromotive force, change of length, and change of resistance.

The fact that tension does not influence either the Hall effect or the Nernst effect indicates that the causes which operate to produce these effects are very unlike those which cause the transverse change of thermoelectromotive force or the transverse change of resistance. If these changes of resistance, length, and thermoelectromotive force are attributed to the distortion of the atoms under tension and magnetization, the observations reported here on the Hall effect and the Nernst effect indicate that these effects are produced by the action of the magnetic field on quasi-free electrons. If such were the case it is easy to see that the magnitudes of these effects might be independent of the tension acting on the plate.

PHYSICAL LABORATORY,
OHIO STATE UNIVERSITY,
January 29, 1923

THE SENSITIVITY OF THE EAR AS A FUNCTION OF PITCH

By Frederick W. Kranz

Abstract

Sensitivity-frequency curves as determined by continuously varying the pitch for different intensity levels.—The threshold sensitivity curve for audition may be determined by varying the intensity at many different pitches, or by varying the pitch at many intensities, noting the ranges of pitch which are audible for each intensity. The latter method enables irregularities in the curve to be more easily and surely determined. In these experiments, a thermophone actuated by current from a vacuum tube oscillator was used, the pitch being controlled by means of a continuously varying inductance, and the threshold sensitivity curve for the frequency range of 360 to 3000 per sec. was determined by the use of successive levels of intensity having an intensity ratio of 2:1. Curves were obtained for *thirty normal ears. They show remarkable individual irregularities*, not only being different for different individuals, but often for the two ears of the same person. In several cases the sensitivity changes by a factor of 200 to 1000 with a change of pitch of a semi-tone. An acceptable theory of the mechanism of audition must explain such abrupt changes. The *average sensitivity* increases from $10^{-7.2}$ for 360 to an approximately constant value of $10^{-8.6}$ ergs/cm²/sec. for frequencies above 1300 per sec.

MANY investigations have been made of the sensitivity of the human ear and of the difference in sensitivity for different pitches.[1] The subject is of importance from the standpoint of the sensitivity of the ear as a piece of physical apparatus and because of the bearing of the results on theories of the mechanism of hearing, besides the medical diagnostic value of tests for deficiency in hearing. The sensitivity of the ear can best be expressed in terms of the minimum sound intensity which is audible. The number scale here used for expressing sensitivity is the logarithm to the base 10 of the reciprocal of the minimum intensity necessary for audition; thus sensitivity $= \log_{10} 1/J$, where J is the intensity expressed in ergs per square centimeter per second.

The greater portion of the apparatus used in the present work was similar to that described in a recent paper by the author in this journal.[1] A thermophone was used as a source of sound, this consisting of a thin

[1] The most extended of these investigations are: Zwaardemaker and Quix, Arch. Anat. Physiol.; Physiol. Abt., Supp., p. 367, 1902; Wien, Arch. f. ges. Physiol. **97**, 1, 1903; Dean and Bunch, Laryngoscope, August, 1919; Minton, Phys. Rev. **19**, 80, 1922; Lane, Phys. Rev. **19**, 492, 1922; Fletcher and Wegel, Phys. Rev. **19**, 553, 1922; Kranz, Phys. Rev. **21**, 530, May 1923.

strip of platinum mounted in a small telephone receiver case held tightly to the ear of the observer. The sound is produced by expansion of the air caused by the periodic heating of the platinum strip by an alternating electrical current flowing through it, this current being supplied by a vacuum tube oscillator. The circuit arrangements are shown in Fig. 1. The pressure changes produced in the ear cavity were obtained by the use of the formula given by Wente[2] which involves the frequency and amplitude of the currents used and the constants of the thermophone. The corresponding sound intensities were calculated from the values of the pressure changes.

In determining the limit of audibility as a function of frequency, it is conceivable that either one of two procedures may be used. The fre-

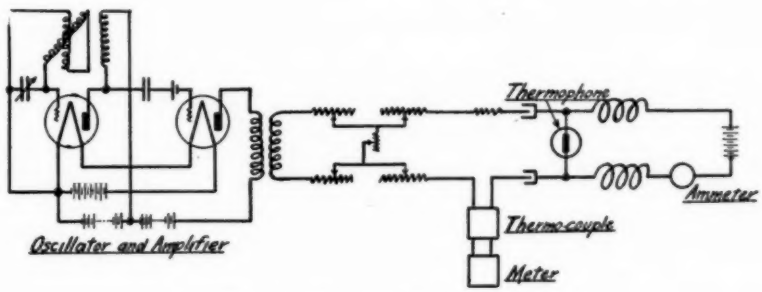

Fig. 1. Diagram of apparatus.

quency may be kept constant and the intensity varied continuously or in small steps until the limit of audibility is reached, and by taking different frequencies successively, the required curve may be obtained point by point. This indeed has been the procedure used in all of the work on ear sensitivity in which the actual ratios of the energies at different frequencies have been obtained. It is clear however, that there must always remain an uncertainty as to what is the nature of the curve between the discrete frequencies used.

The other possible method is to vary the frequency back and forth over a considerable range, the intensity being changed by successive increments. Thus for different intensities near the low limit, different portions of the frequency range will in general be audible. By a suitable choice of the intensity increments, the desired curve of relationship between frequency and necessary intensity for audibility may be determined as accurately as is desired, and the amount of assumption involved in the completed curve will be known. Any peaks of dips in the curve which

[2] Wente, Phys. Rev. **19**, 336, 1922

extend over a narrow range of frequencies will be easily detected by this method, while with the use of discrete frequencies it would require a prohibitive amount of time and work to take a sufficient number of points to locate and measure all the possible peaks and dips in any extended range of frequencies. Seashore, Dean and Bunch[1] have worked on this second method, obtaining a continuous change of frequency over a considerable range by the change in speed of rotation of an electrical generator, the resulting current being put through a telephone receiver. Various shunts were put across the telephone receiver to give various levels of intensity. By this method deficiencies in audition over a portion of the range can in general be detected. No attempt was made to get absolute values of intensity, and indeed actual ratios of intensities at different frequencies were not known because of the unknown characteristics of the telephone receiver and of the generator.

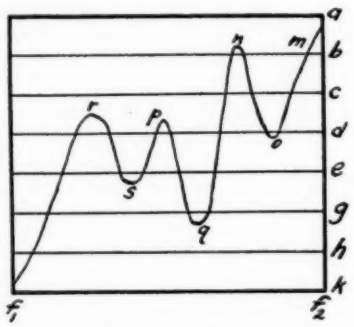

Fig. 2. Diagrammatic curve.

In the present experiment, the second of the two methods was used, the frequency change being effected by a change in the inductance in the oscillating circuit of the vacuum tube oscillator. The inductance coil was made in sections which could be separated, these being mounted on a sliding device equipped with a pointer traveling over a scale for calibration purposes. It was found possible to vary the frequency satisfactorily over a range of a little less than an octave by thus changing the inductance, and different ranges of frequency were obtained by varying the capacity of the oscillator circuit. Several slightly overlapping ranges were used, which together covered the frequencies from 360 to 3000 per sec. It may be remarked that frequencies above this latter figure are of small practical importance as far as speech is concerned.

The principle of the present method is illustrated in Fig. 2. Suppose the form of the sensitivity-frequency curve is as shown, between the frequencies f_1 and f_2. The higher sensitivity of course corresponds to the

less intensity. Let the levels of intensity used be as shown by the horizontal lines *a* to *k*. At the intensity level *a*, nothing is audible as the frequency is varied from f_1 to f_2. At the level *b*, parts of the frequency range corresponding to portions *m* and *n* of the curve are audible. At the level *d*, peaks *p* and *r* are noticeable and the gap at *o* is narrowed. At level *e*, the dip *o* has disappeared and all of the frequency range is heard from f_2 to a point on the *nq* slope. At level *g*, the gap *s* is no longer found and at level *h*, all of the frequency range from f_2 nearly to f_1 is audible. So it amounts to taking horizontal sections of the sensitivity-frequency curve and these sections can be as numerous as the experimentor wishes and so the curve may be determined with as great a degree of accuracy as is desired.

The procedure of the test was to have the subject control the frequency by means of a handle on the inductance coils. The current was first reduced by the operator until the sound was insufficient to be audible to the subject at any point in the range being used. The current was then increased in steps with a ratio of approximately 1.4 : 1, the corresponding intensity changes having ratios of 2 : 1; that is the intensity was doubled at each change. After each current change, the subject varied the inductance and determined what portion of the range he could hear, the alternating current values at the limiting frequencies and sometimes at intermediate frequencies being read by the operator on the thermal ammeter which was always in circuit. The frequencies were then read from a preliminary calibration of the inductance scale. The current was increased by steps until all of the range was heard.

Results

Figs. 3 and 4 show the sensitivities of the ears of some of the individuals tested by this method. The observations on the left and right ears of the individual are marked as L and R respectively. All of the people examined would be rated as normal hearing people in the popular sense of the term and had never experienced any difficulty in hearing.

The absolute values of sensitivity are found to vary between 10 and 6 in the range of frequencies used. This means that intensities of from 10^{-10} to 10^{-6} ergs/cm^2/sec. are audible. Of the small variations shown in all of the curves, many are undoubtedly real although the accuracy of the measurements is not in general much better than 0.3 in logarithmic sensitivity due to the magnitude of the intensity increments used in these tests. In any case the small variations probably do not have much significance. It is seen that there are no pronounced peaks or depressions of sensitivity common to all ears although a decrease at the lower end is

quite well established, in agreement with previous work of the author and others.

Fig. 3A is of a type which shows no irregularities of any consequence in the frequency range covered. Fig. 3B represents the sensitivity of an individual having no mastoid cavity on the right side. The effect on the hearing is certainly not great, for although below 1000 per sec. the right ear is somewhat less sensitive than the left, the difference is not sufficient

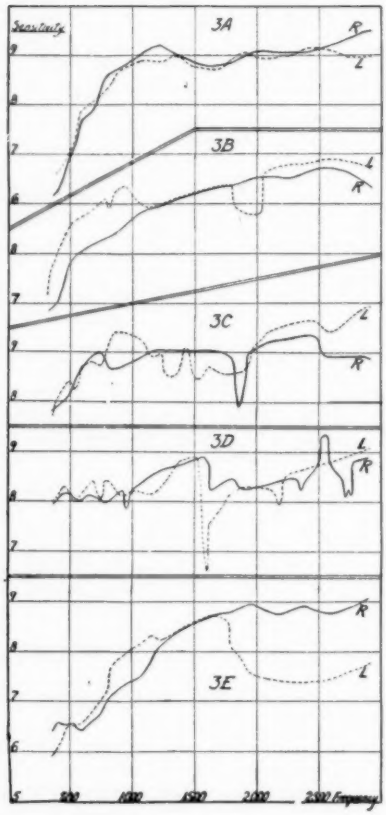

Fig. 3. Sensitivity curves for individual normal ears.

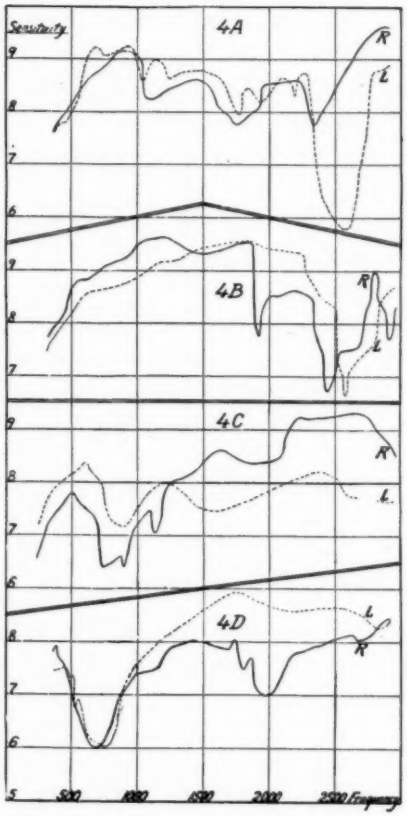

Fig. 4. Sensitivity curves for individual normal ears.

to be of any practical importance. The left ear shows a depression of small consequence in the neighborhood of 2000. Fig. 3D shows a similar depression at a frequency of 1600 which is very narrow in the lower part. On the low frequency side of this depression, the change in sensitivity is quite abrupt, with a sensitivity change of 2.3 or a change in intensity by a factor of 200 in passing over a frequency change of 80 cycles, which is

here a little less than semi-tone. This dip is a good illustration of the type of sensitivity variation which would probably not be located at all by the method of tests with discrete frequencies, and if located it would be very difficult to determine its limits or indeed to locate the lowest point of the sensitivity. The other figures show depressions over part of the frequency range, the width and depth of the depressions varying considerably. Rather broad depressions, coming back up to the average height on both sides, are shown by several of the curves, one of the most pronounced of this character being in Fig. 4A. The depth of this depression corresponds to a change in logarithmic sensitivity of 3, or an intensity ratio of 1000. Fig. 3E shows a diminished sensitivity for all frequencies above 1800. Fig. 4B shows rather narrow holes within fairly wide areas

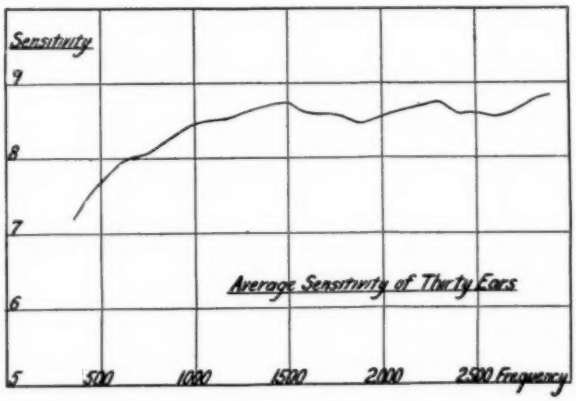

Fig. 5. Average sensitivity of thirty ears.

of depression. Figs. 4C and 4D show deficiencies in sensitivity for the lower part of the frequency range, the depressions in Fig. 4D being especially marked and extending from 400 to at least 1000, an interval of more than an octave, and involving both ears. Fig. 5 shows the average curve of sensitivity for the thirty ears which were tested, attained by averaging the sensitivities as above defined.

It may be noted that in some cases of considerable deficiency in sensitivity for one ear of an individual, there is a tendency toward deficiency for the other ear in the same range. This is not true for all of the individuals however.

Discussion

The abruptness of the change in sensitivity in passing over the frequency range is in many cases very marked and is probably the most

striking feature of the results here presented. An explanation of the abruptness of these changes in sensitivity must be included in any comprehensive theory of the mechanism of audition. Pictorially it would seem to require the physical existence of a large number of elements (1) which are each concerned with the transmission of only a very narrow range of frequencies, (2)which exist either in the inner ear or in a possible nerve cable from the ear to the brain or conceivably in the brain itself or in all three places, and (3) which are of such a nature that individual e'ements may be quite severely injured without seriously affecting neighboring elements. If, as many theories of audition suggest, a differentiation between frequencies is made in the inner ear, it is hardly reasonable to suppose that the impulses are again compounded to be sent to the brain over a single nerve, and so a bundle or cable of nerves would be needed for the connection between ear and brain. It is conceivable that the nature of the different strands of this cable are such as to accentuate the differentiation between frequencies originally made, perhaps not so very sharply, in the inner ear. At any rate, injury to individual strands of this cable or to the terminal apparatus on either end would, if the frequency discrimination were sufficient, serve to explain the abruptness of the changes in sensitivity which are found.

As for the method here used, one advantage is that absolute values of sensitivity are found, but perhaps the unique advantage is that no assumptions are made as to the continuity of the sensitivity over any part of the frequency range covered, this distinguishing it from all methods using tests at discrete frequencies. With the latter type of test, the resulting curve may take a wide variety of forms depending on the particular frequencies chosen for the tests. The use of a continuous frequency range makes possible the easy and accurate testing of the sharp breaks in sensitivity mentioned above, which would be very difficult by any other method. The method thus seems to make possible more thorough and accurate analyses of audition than any heretofore used. The thermo-phone serves well in testing normal or nearly normal ears, while a properly calibrated instrument of greater efficiency such as an electromagnetic type with the natural frequency of the diaphragm above the range to be used, would be better suited to the testing of more deficient ears.

RIVERBANK LABORATORIES,
GENEVA, ILLINOIS,
January 8, 1923

EFFECT OF CONICAL HORNS ON THE INTENSITY OF SOUND EMITTED BY AN ORGAN PIPE

By J. H. Cloud

Abstract

Effect of conical horn on the intensity of sound emitted by an open organ pipe.—In a room lined with hair felt one inch thick to reduce resonance effects, readings taken with a Webster phonometer showed that while the horn (50 cm long, 6° flare) doubled the intensity, it acted merely as a resonator and did not concentrate the energy in front to any measurable extent. Outdoor experiments gave the same result except that the intensity was increased by only one half.

Webster phonometer with a disk supported by wires under tension, is a convenient portable instrument, as sensitive as the ear to the pitch to which it is tuned, but it shows a very sharp resonance to the natural frequency of the disk and this selectivity limits its usefulness.

Rayleigh disk phonometer is described. It may be used to measure the absolute energy density of sound.

THE commonly accepted explanation of conical megaphones is that sound waves are reflected by the walls of the tube and thus sent out in some definite direction. Similarly, conical mouth pieces of telephones are supposed to concentrate the waves upon the diaphragm. However, photographs taken by Dr Foley, of sound waves entering conical tubes show that the waves are reflected so as to be sent back out of the horn at the end where they entered. This indicates that the so-called "condensing power" of horns having a large angle of flare may be partly imaginary.

It was thought desirable, therfore, to investigate the effect of a conical horn on the sound emitted by an organ pipe, both as to the intensification of the sound and as to the directing action.

The source of sound was an ordinary organ pipe 52.6 cm long, blown at constant pressure. The receiving apparatus was a Webster phonometer, except for some experiments for which a Rayleigh disk phonometer was used.

The Webster phonometer[1] has a mica disk supported by means of three symmetrically placed wires in a vertical plane. Attached to the center of this disk is a brass pin ground to a point, which presses against a flexible steel strip which carries a minute concave mirror and is supported

[1] Webster, Boltzmen Memorial Volume 1904; King, Phil. Trans. **218** (1919)

in a vertical position by means of a separate frame. The circular metal frame supporting the mica disk forms one end of the ordinary cylindrical resonator, whose length may be varied by drawing out the inner telescoping tube. The image of a lamp filament is focused by the concave mirror on the scale of the eye-piece by which readings are taken. When a train of sound waves of suitable frequency falls upon the resonator the motion of the mica disk is transmitted to the mirror and the filament image, otherwise sharp, widens out into a broad band of light whose width may be read from the scale. It may be of interest to note that when an ordinary small siren was used as a source, the broadened band showed a number of flutings, doubtless due to overtones.

The phonometer showed sharp resonance to the natural frequency of the disk, regardless of the position of the resonator. For instance when a Stearn's variometer was sounded continuously nearby and the pitch gradually changed, readings such as the following were obtained:

Pitch:	160	202	210	221	225	226	227	300
Reading:	0.1	2.5	4.0	10	>10	10	6.0	0.1

By changing the tension in the wires supporting the mica disk, the pitch to which the phonometer reponds most vigorously could be varied from about 150 to 320. As might be expected, change in temperature alters the tension and therefore the pitch to which the phonometer is most sensitive.

Effect of the conical horn. For the indoor readings, an attempt was made to minimize reflection and the resulting interference effects by covering the floor, walls and ceiling of a room 12 by 18 feet with hair felt one inch thick.

The organ pipe was clamped in a horizontal position in the center of the room and phonometer readings were taken at points A, B, C, and D, 45° apart on the circumference of a circle drawn with the mouth of the organ pipe as center. Sets of readings were taken at various distances from the source and with various air pressures. One set is given in Table I. A is directly in front of the horn, C directly behind it. The results show that the amplification ratio for this particular horn is about 2, and that this ratio is practically the same behind the horn as in front of it.

TABLE I

Effect of a conical horn; indoor results

Position	With horn	Without horn	Ratio
A (front)	4.0	2.1	1.9
B	4.1	2.0	2.0
C (back)	4.0	2.0	2.0
D	5.2	2.1	2.5

It appears, therefore, that for continuous sounds of this type the horn does not concentrate the sound energy in front of the horn by reflecting the waves from the conical walls, but acts as a resonator to the source, increasing the amplitude of the wave and hence the loudness of the sound in all parts of the room.

By means of a rubber hose, air was conducted to a point on the campus 200 feet from any building and the experiments with the horn repeated. The readings were more nearly uniform on the athletic field away from trees and buildings but owing to a lack of air pressure there, the readings were inconveniently small. An increase in loudness and a change in the quality of the note could be detected by the ear when the horn was inserted but readings taken directly in front of the horn were only slightly greater than those taken at the same distance but at one side or behind the horn. Table II is a sample of many sets of readings.

TABLE II

Effect of a conical horn; outdoor results

Distance	Front	Side	No horn	Distance	Front	Side	No horn
5 ft	7.2	7.0	5.1	150 ft	.4	.3	.3
10	4.5	4.5	3.0	200	.4	.4	.2
30	1.8	2.0	1.0	300	.3	.3	.0
60	1.2	1.1	.6	400	.2	.1	.0
100	.6	.6	.3	500	.1	.1	.0

The effect again seems to be one of resonance rather than concentration of energy in front of the horn. In the same way that the box on the violin and the sounding board on the piano enable those instruments to emit stronger waves than would be sent out by the strings alone, so here the horn increases the amplitude of the wave produced by the pipe.

Distribution in intensity around an organ pipe source. For these experiments a *Rayleigh disk phonometer* was used. This instrument had a Rayleigh disk, a silvered cover glass 15 mm in diameter, suspended in the throat of a compound resonator made of two cylindrical metal chambers, 12.5 and 3.2 cm long respectively, and each 4.8 cm in diameter, connected by a tube 8 cm long and 2.8 cm in diameter (see Fig. 1). The opening at the outer end of the large chamber could be varied by means of an iris diaphragm which was surrounded by a flange extending 20 cm beyond the tube.

When the disk is set at 45°, its most sensitive position, the deflection φ, if small, is directly proportional to the energy per unit volume of the vibrating medium of the resonator.

$$\varphi = C(\tfrac{1}{2}\rho v^2) \qquad (1)$$

The absolute value of the energy may be computed if C is known. C was determined by measuring the period of the disk and fiber with and without a short cylinder whose moment of inertia was known. Then to pass from the energy density in the resonator to that outside we use the Helmholtz factor $2R^3/\pi^2 S$.

To eliminate reflection and interference effects, measurements were made outdoors. A level tract of land covered with grass was selected, with neither buildings nor trees near. It was found impossible to obtain trustworthy readings when a strong wind was blowing, but on the calmest days the zero reading of the spot of light on the scale was fairly constant and readings could be repeated within about 5 per cent. The whole apparatus was protected from the wind by means of a light frame covered with cheese cloth, and four thicknesses of the same material

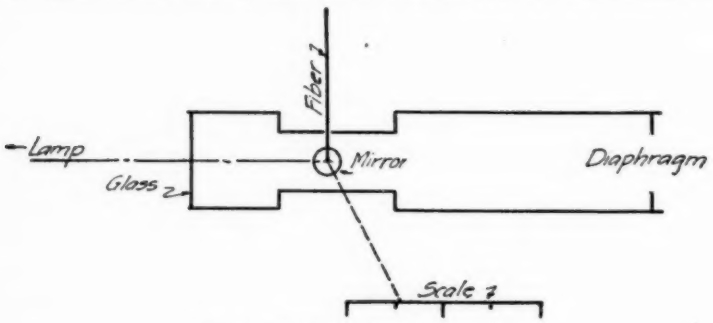

Fig. 1. Rayleigh Disk Apparatus

were loosely placed over the mouth of the resonator and held in position by means of rubber bands. These layers of cheese cloth did not appreciably diminish the response of the resonator.

With a radius of ten feet, a circle was drawn with the resonator as center. The circumference was divided into arcs of 45° each, the points of division being lettered A, B, C, D, E, F, G and H, beginning directly in front of the resonator. Readings were taken when the pipe was blown at A, B, C, and so on in succession around the circle. The radius of the circle was then increased to 20, 30, 40 and 50 feet in succession. This was done several times and the average readings are recorded in Table III.

Variation of intensity of sound with distance over flat ground. Tables II and III show that the intensity does not decrease as fast as the inverse square but more nearly as the inverse first power of the distance. The exact law depends, of course, in the reflecting power of the ground and on the elevation of the source and receiver.

Absolute efficiency of an organ pipe. By evaluating the constant C in Eq. (1) and measuring the volume and pressure of the air used to blow

the organ pipe, the efficiency of this source at a distance of 40 feet was calculated isothermally and found to be only .005 per cent. Of course the energy in the upper partials was not measured.

Interference effects in a closed room. In a room 12 by 16 feet with a 12 foot ceiling, the resonator was placed in a fixed position and the organ pipe moved around it. Positions were found in which the pipe produced almost no effect upon the resonator, due to interference. Similar results were obtained in a larger room with the Webster phonometer, only in this case the phonometer was carried around. As many

TABLE III

Distribution of intensity around an organ pipe

Radius in feet	Scale deflection in cm								
	A	B	C	D	E	F	G	H	Mean
10	28	28	26	25	25	26	25	28	26.4
20	12.5	12	12	10	10	10	11	12	11.2
30	7.5	7	6	6	6	6	6	7	6.4
40	4	4	3	3	3	3	4	4	3.5
50	2	2	1	1	1	1	1	1	1.2

as thirty minima or regions of silence were located and marked on the floor of the room. They showed considerable regularity, resembling the interference patterns seen on the surface of a liquid produced by reflection from the walls of the vessel. The average distance between these points of silence was about 80 cm, just half the length of the wave produced at that temperature. These points of minima and maxima could be distinguished with the unaided ear. A long step ladder was placed in the room by which the phonometer could be carried step by step from floor to ceiling, and minima and maxima were again located, showing the presence of three-dimensional nodes and loops in satisfactory agreement with Sabine.[2]

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[2] Sabine, Collected Papers on Acoustics, pp. 166 and 233

THE MOLECULAR SCATTERING OF LIGHT IN LIQUID MIXTURES

By J. C. Kamesvara Rav

Abstract

Molecular scattering by mixtures of carbon bisulphide and acetone. —*The intensity of light* scattered transverse to the primary beam by various dust-free mixtures is found to be much higher than is predicted by Einstein's formula which takes into consideration scattering due to concentration fluctuations alone, but to agree quantitatively with the stricter theory developed by C. V. Raman which takes into consideration also the scattering due to density fluctuations and the orientation scattering due to the anisotropy of the molecules. The *polarisation* of the transversely scattered light has also been determined and is found to agree with the formula given by Raman and Ramanathan. These results tend to confirm the *Raman theory*.

1. Introduction

Smoluchowski[1] and Einstein[2] developed a theory of the scattering of light in liquid mixtures based on the conception that spontaneous local fluctuations of composition occur in the mixture and cause optical inhomogeneity. Einstein's formula for this effect (which we shall refer to in what follows as the concentration-scattering), was experimentally verified by Fürth[3] and Zernike[4] for mixtures in the immediate vicinity of the critical solution temperature. That other effects besides the concentration-scattering must be taken into account in order to explain the observed phenomena in the general case was pointed out by C. V. Raman.[5] The more complete theory[6] includes also the density-scattering, and the orientation-scattering, that is, the scattering of light due to the local fluctuations of density of the mixture regarded as a substance of invariable composition, and the scattering due to the anisotropy of the molecules and their varying orientation.

The density-scattering Ω_1 in a transverse direction is completely polarised, and per unit of volume and at unit distance is

$$\Omega_1 = \frac{\pi^2}{18} \frac{RT\beta}{N\lambda^4} (\mu^2-1)^2 (\mu^2+2)^2, \qquad (1)$$

[1] Smoluchowski, Ann. der Phys. **25**, p. 219 (1908)
[2] Einstein, Ann. der Phys. **33**, p. 1295 (1910)
[3] Fürth, Wiener Berichte **124**, p. 577 (1915)
[4] Zernike, Thesis, Amsterdam, 1914
[5] Raman, Nature, July 1922, p. 77
[6] Raman and Ramanathan, Phil. Mag. Jan. 1923, p. 213

where N, T and R have the same significance as in Kinetic theory, β is the isothermal compressibility, μ is the refractive index of the mixture and λ is the wave-length of the light used. The concentration scattering Ω_2 is also completely polarised and is with sufficient accuracy given by the expression

$$\Omega_2 = \frac{2M_2\mu^2\,(\delta\mu/\delta k)^2}{N\lambda^4 m_1 \delta \log\, p_2/\delta k}, \tag{2}$$

where m_1 is the mass of the first component in unit volume of the mixture; M_2 is the molecular weight of the second component in the gaseous phase; k is the ratio of the mass of the second component to that of the first, and p_2 is the partial vapor pressure of the second component.

The orientation scattering consists principally of unpolarised light $4\Omega_4$ which is equally divided between the two perpendicular directions of vibration and is given by

$$4\Omega_4 = n_1x_1 + n_2x_2 \tag{3}$$

where x_1 and x_2 are constants characteristic of each kind of molecule in the mixture and n_1, n_2 are the numbers of each kind in unit volume. We also have

$$\gamma = 2\Omega_4/(\Omega_1+\Omega_2+\Omega_3+2\Omega_4) \tag{4}$$

where γ is the ratio of the intensity of the weak to the strong component of polarisation in the transversely scattered light. Ω_3 is the polarised part of the orientation scattering and will, in what follows, be neglected, being generally quite small. Knowing the values of γ corresponding to the case in which the liquid contains only one component or the other, the values of x_1 and x_2 can be determined and the values of γ for any other composition can be calculated. The total intensity of scattered light $\Omega_1+\Omega_2+2\Omega_4$ and the state of its polarisation γ can thus be predicted if the requisite physical constants for the mixture are known.

Some observations on the scattering of light by liquid mixtures of carbon bisulphide and ether, benzene and normal hexane, normal hexane and cyclohexane were made by Martin and Lehman.[7] Raman and Ramanathan have shown that there is a general agreement between their results and the indications of the theory; but a complete verification was not found to be possible, as the compressibility and vapor pressure data are not available for those mixtures. With a view to making a detailed verification, the present work was taken up. Fortunately there are some liquid mixtures for which the compressibility and refractive indices and partial vapor pressures are all known. One such case is that of

[7] Martin and Lehman, Journal of Phys. Chemistry, **26** (1922)

mixtures of carbon-bisulphide and acetone, and this case was therefore chosen for the present investigation.

2. Experimental Procedure

The chief difficulty in the work is to prepare perfectly dust-free liquids. For this purpose, Martin and others have made use of vacuum distillation in spherical bulbs, but this is not suitable for the most accurate determinations, owing to the fact that the bulbs act as lenses and cause the pencils of light passing through to converge, thus leading to error in the photometric work. In their work on mixtures of carbon-bisulphide and ether etc., Martin and Lehman used a very elaborate form of apparatus consisting of a cross tube of pyrex glass with flat windows fused on, with a special arrangement for mixing the liquids in a vacuum. In the present investigation a much simpler form of apparatus has been used. The mixtures to be studied were contained in cut-glass bottles having flat sides and were rendered dust-free in the following manner. A tube is fitted into the mouth of the bottle with an air-tight ground joint and is connected with a bulb, as shown in Fig. 1. The whole apparatus is thoroughly cleaned and the liquid is put in the bulb, which is heated on a bath and the bottle is put in cold water. After the distillation, the bottle is rinsed with the liquid by thoroughly shaking the bottle, and the liquid is transferred back into the bulb. By repeating this process five or six times, mote-free liquid is obtained. In the final distillation, the whole of the liquid must be distilled into the bottle. 30 cc of the mixture are taken and five different mixtures are prepared.

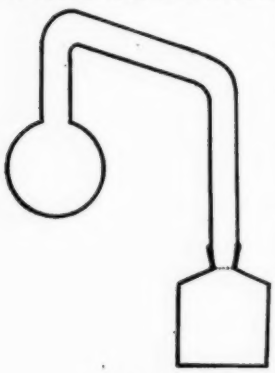

Fig. 1

For measurements of the intensity of scattered light, a second bottle containing carbon-bisulphide is used as a standard of comparison. The two bottles are set side by side and one side of each bottle is painted jet black externally, to secure a good background. A pencil of sunlight condensed by means of a long focus lens, passes in succession through the two bottles and gives horizontal blue tracks in the liquids. The relative intensities of the two tracks is determined with the aid of an Abney rotating-sector photometer. In order to eliminate errors arising from the reflection at the surfaces of the bottles, from the slight convergence of the illuminating beam and other causes, the ratio of the intensities when both bottles contained carbon-bisulphide was determined, and it was found that a correction of +5 per cent had to be applied to the intensity

of the track in the second bottle. For the small thicknesses of the pure liquids and mixtures used, the effect of absorption on the scattered light is quite negligible. Indeed the color of the track observed in pure liquids and in the mixtures was found to be blue, and no difficulty was experienced in making the intensity measurements. Care was taken to see that the liquids were exposed only for a short time to avoid any decomposition of the liquid by light when the observations were taken.

Polarisation measurements are made by a double image prism and a nicol. The double image prism gives two images of the track, polarised respectively in horizontal and vertical planes. By rotating the prism, the two images can be brought into a line. By rotating the nicol placed immediately behind the prism, two positions may be found in which the images appear of equal intensity. If 2θ be the angle between these positions of the nicol, then $\gamma = \tan^2\theta$ where γ is the ratio of the weak component to the strong.

3. Calculated and Observed Values

In the calculations, carbon-bisulphide is taken as the first component and acetone as the second. All data (observed and calculated) refer to 30°C. In calculating the density and concentration scattering the common multiplying factor $1/N\lambda^4$ is omitted. The compressibility data are taken from Cohen's Piezo-Chemie. The compressibilities for different concentrations are given in the following table.

Table I

Compressibilities of mixtures of CS_2 and acetone

Liquid:	CS_2	k=0.191	k=0.498	k=0.975	k=3.41	Acetone
$\beta\times10^6$:	85.9	86.7	93.7	103.4	107.2	110.7

The variation of refractive index with concentration is calculated from the following formula for the F line.

$$\frac{\epsilon-1}{\epsilon+2}\cdot\frac{1}{\rho} = \frac{\epsilon_1-1}{(\epsilon_1+2)\rho_1}f_1 + \frac{\epsilon_2-1}{(\epsilon_2+2)\rho_2}f_2,$$

where ϵ, ϵ_1, ϵ_2 are respectively the squares of the refractive indices of the mixture, and of the two components; ρ, ρ_1, ρ_2 are respectively the densities of the mixture and of the two components; f_1 and f_2 are the fractions of the masses of each of the two components in the total mass of the mixture. This method of calculation is justified by the fact that the calculated values for the D line agree very well with the observed values as given in the Landolt and Börnstein Tables. The values of ϵ for different concentrations are given in Table II.

Though the incident light is not homogeneous, as we are concerned only with the ratios and not with the absolute values, we shall not be far from right if we take the refractive indices corresponding to the *F* line as representative of the whole.

TABLE II

Square of refractive index μ_F for mixtures of CS_2 and acetone

Liquid: Acetone										CS_2
$k=$:	∞	9	4	2.3	1.5	1	½	¼	⅑	0
$\epsilon=\mu_F^2$:	1.860	1.906	1.958	2.014	2.092	2.152	2.292	2.430	2.570	2.732

From Tables I and II the compressibilities and refractive indices for the required concentrations are obtained by interpolation. Knowing R to be equal to 83.15×10^6 c.g.s. units, the values of $\Omega_1\times N\lambda^4$ are calculated.

For calculating the concentration-scattering, the variation of log p_2, where p_2 is the partial vapor pressure of the second component (acetone in this case) with concentration, is given in the following table (calculated from the Landolt and Börnstein Tables).

TABLE III

Partial vapor pressure of acetone in mixtures of CS_2 and acetone

k	: 11.47	5.534	3.343	1.998	1.416	1.118	0.943	0.771	0.569	0.476	0.323	0.159	0.068
log p_2-12 :	.9965	.9406	.8828	.8119	.7700	.7338	.7167	.6838	.6421	.6127	.5771	.3885	.0098

The variation of ϵ and k is given in Table II. The values of $\delta \log p_2/\delta k$ are found by the usual method after drawing a graph with k as abscissa and log p_2 as ordinate. In a similar manner, $\delta\epsilon/\delta k$ is found from another graph. Then the values of $\Omega_2 N\lambda^4$ are calculated. The orientation scattering is first calculated for acetone and carbon bisulphide from (4) after knowing the ratio of the two components of polarisation from the observed values. Since the orientation scattering is proportional to the number of molecules of each component, the variation of $4\Omega_4$ with

TABLE IV

Calculated and observed intensities for the transversely scattered light

Liquid	Volume of CS_2 (percent)	Concentration k	Density scattering $\Omega_1\times N\lambda^4$	Concentation scattering $\Omega_2\times N\lambda^4$	Orientation scattering $4\Omega\times N\lambda^4$	Total Scattering Ω	$\frac{\Omega}{\Omega(CS_2)}$ Calc.	obs.
Acetone	0		16.8	0	13	30	0.066	0.07
A	16.7	3.084	23.0	29	73	125	0.28	0.25
B	33.3	1.234	30.1	131	133	294	0.65	0.64
C	50.0	0.617	37.4	224	193	454	1.00	1.00
D	66.7	0.308	45.6	291	253	590	1.30	1.29
E	83.3	0.123	58.0	140	313	511	1.12	1.11
CS_2	100		80.5	0	373	453	1.00	1.00

k will be linear and is easily calculated. The last two columns of Table IV give the ratio of the total scattering from the mixture to the total scattering from CS_2 both as calculated and as observed.

A graph (Fig. 2) gives the intensity as a function of the percentage volume of carbon bisulphide. The dotted curve shows the observed values and the other one shows the calculated values.

In both Table IV and Fig. (2), one sees a fairly good agreement between the calculated and observed values. A similar agreement is also found in the case of polarisation measurements. Knowing the values of γ for acetone and carbon bisulphide, obtained by direct observation, the values of γ for the mixtures are calculated from (4), neglecting

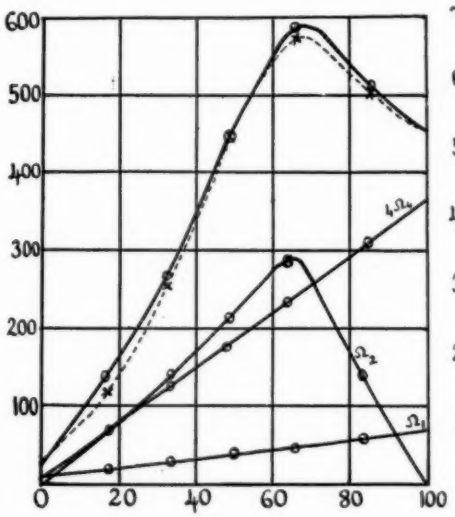

FIG. 2

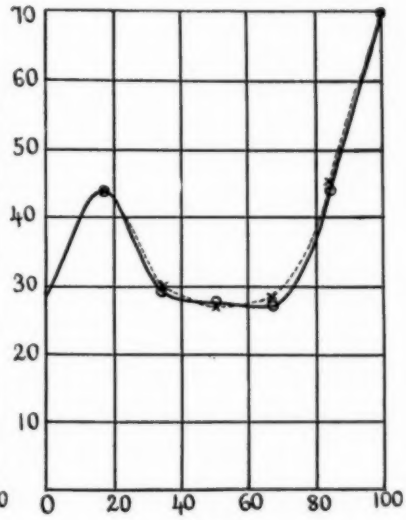

FIG. 3

FIG. 2. Scattered intensity as a function of percentage volume of CS_2.
FIG. 3. Polarization (100γ) as a function of percentage volume of CS_2.

Ω_3. The calculated and observed values are given in the following table.

TABLE V

Polarization of light transversely scattered from mixtures of CS_2 and acetone

Liquid	Volume of CS_2 (percent)	k	100γ Calc.	Obs.
Acetone	0		28.0	28.0
A	16.7	3.084	43.5	43.5
B	33.3	1.234	29.5	30.0
C	50.0	0.617	27.5	27.0
D	66.7	0.308	27.0	28.0
E	83.3	0.123	44.4	44.0
CS^2	100.0		70.0	70.0

A graph Fig. (3) shows γ as a function of the percentage volume of carbon bisulphide.

In conclusion, the author wishes to record his best thanks to Prof. C. V. Raman, under whose guidance the above work was carried out, for his kind and helpful interest in the investigation.

210, Bowbazaar Street,
Calcutta, India.
December 23, 1922.

ON THE COLOR OF THE SEA[1]

By Was. Shoulejkin

Abstract[2]

Color of seas and lakes cannot be explained either by (1) the intrinsic color of water due to selective absorption $f(\lambda)$, or by (2) the Rayleigh scattering by microscopic particles or bubbles of gas $\frac{1}{2}\alpha/\lambda^4$, alone. A combination of these two causes, however, together with (3) selective reflection $\varphi(\lambda)$ by larger pa ticles (clay, plank ton, etc.) and (4) light reflected from the sky, seems to be adequate, if the effect of waves is taken into account. The *general theory* is developed, and then, using experimentally determined values of the selective reflection $\varphi(\lambda)$ for a brown clay suspension, curves are computed for various va'ues of the propo: tion of such pa·ticles β, and for the scattering coefficient α, which give resultant colors varying from green to brown, as determined by o; tical synthesis. By the use of a colloidal solution of rosin in alcohol colored with Redulin blue, a *model of the sea* was made which gave spectrophotometric curves agreeing closely with the theory. The *theory of the Secchi disk* is given and the relation between the coefficient of diffusion α and the maximum depth at which the disk is visible. Coefficients computed from disk observation for various lakes agree with those obtained from the spectral distribution curves of Aufsess.—G. S. F.

THE numerous attempts to explain the color of seas and lakes have usually proceeded from two principal assumptions. One group of authors ascribe the origin of this color to the intrinsic color of water due to the strong absorption in the water of rays of the yellow and red parts of the spectrum and to the feeble absorption of the blue and violet rays, noted by Bunsen and finally definitely established by Spring. Then after the work of Lord Rayleigh[3] on the color of turbid media was published, other authors tried to explain the color of the seas entirely by the scattering of light by fine particles suspended in the water as a result of which they thought the diffused light coming from the water acquires a blue color. But such an explanation has not given satisfactory results, quantitatively nor even qualitatively, and O. v. Aufsess,[4] who applied methods of spectrophotometry to such researches, was obliged to discard it.

[1] Communicated to the Scientific Institution of Moscow, October 8 and 15, 1921.

[2] This abstract was prepared by an editor and has not been verified by the author.

[3] Lord Rayleigh, Phil. Mag (4) **41**, 1871; (5) **12**, 1881; (5) **47**, 1899.

[4] O. v. Aufsess, Physikalische Eigenschaften der Seen; Die Farbe der Seen (Dissertation) München.

From observations of the coefficient of absorption in different parts of the spectrum for a series of specimens of water taken from different lakes, Aufsess concludes that the diffusion of light by the suspended particles is a phenomenon of the second order, and that all gradations of color in seas and lakes are caused by coloring materials mixed with the water, which produce the dependence of the coefficient of absorption upon the wave-length shown by curves calculated by him.

It is easy to show that neither the theory of Rayleigh in its pure form, nor the supposition of Aufsess, is justified by the facts. The first would lead to white coloring for the sea and the second to perfectly black, in case we should try to get quantitative results.

This work is an attempt at a quantitative investigation, as far as possible, of all the fundamental phenomenona connected with the transmission of light through sea water. Such an investigation permits us to obtain the spectrum of the diffused light emitted by the sea, for a series of typical cases.

1. *Diffused interior light.* Let us suppose that upon the surface of the sea there falls a certain quantity of radiation, depending, generally speaking, upon the height of the sun and illumination of the sky. Let us denote the quantity of energy flowing in through a unit of surface by J_0. Let us consider an elementary horizontal stratum, dz, the distance of which below the surface of the water is z. The quantity of energy flowing in from above will be J and the quantity of energy flowing out downwards $J+dJ$, where dJ is negative. The decrease of energy dJ is caused by two factors, (1) the diffusion of energy in the elementary stratum dz and (2) absorption of energy by the water of this stratum.

If we denote by φ the angle between the ray falling upon an element of volume of the turbid medium and one of the diffused rays emitted in all directions, the energy of this diffused ray, according to Rayleigh, is proportional to $(1+\cos^2\varphi)$. Consequently all particles enclosed inside the stratum dz, will diffuse an equal quantity of energy upwards and downwards from this stratum. Therefore, if $(\alpha/\lambda^4)Jdz$ is the whole quantity of energy emitted by the particles of the stratum, the quantity of energy radiated upwards will be equal to $\frac{1}{2}(\alpha/\lambda^4)Jdz$ where λ is the wave-length and α is the coefficient of diffusion.

The energy absorbed in the water of the stratum dz is also a function of the wave-length and will be equal to $Jf(\lambda)dz$. The total decrease of the flow of energy through unit surface downwards, will be, therefore,

$$dJ = -J\left[\tfrac{1}{2}\frac{\alpha}{\lambda^4}+f(\lambda)\right]dz \qquad (1')$$

We will take into account the absorption of energy by the suspended particles themselves later, in section 4. From this equation it is easy to determine the quantity of energy flowing from above on unit surface of the stratum with the coordinate z

$$J = J_0 e^{-[\frac{1}{2}(a/\lambda^4)+f(\lambda)]z} \tag{1}$$

Remembering that the quantity of energy, radiated by the stratum upwards is equal to $\frac{1}{2}(a/\lambda^4)Jdz$, and denoting it by dI_z, we obtain from Eq. (1)

$$dI_z = \tfrac{1}{2}(a/\lambda^4)J_0 e^{-[\frac{1}{2}(a/\lambda^4)+f(\lambda)]z}dz$$

The light coming out of the sea is emitted by these elementary strata dz, but of course between each stratum dz and the surface of the sea, there lies a stratum of water with the thickness z, the absorption and diffusion in which is determined by formulas analogous to (1′) and (1).

If dI_1 is the quantity of energy that has reached the surface of the sea from the stratum dz, then

$$dI_1 = dI_z e^{-[\frac{1}{2}(a/\lambda^4)+f(\lambda)]z} = \tfrac{1}{2}(a/\lambda^4)J_0 e^{-[\frac{1}{2}(a/\lambda^4)+f(\lambda)]2z}dz \tag{2}$$

As the visible rays of the spectrum do not, practically, penetrate depths of even several hundred meters, the integration of Eq. (2) can be carried out without paying attention to the bottom of the sea, that is within limits from 0 to ∞

$$I_1 = \int_0^\infty \tfrac{1}{2}(a/\lambda^4)J_0 \cdot e^{-[\frac{1}{2}(a/\lambda^4)+f(\lambda)]2z}dz = \frac{J_0}{2}\,\frac{\frac{1}{2}(a/\lambda^4)}{\frac{1}{2}a/\lambda^4+f(\lambda)} \tag{3}$$

It is evident that I_1 forms only one part of the whole energy coming out of the sea. For on the way from the stratum dz to the surface of the sea, part of the element of energy dI_z is scattered downwards. Applying here the same methods as we used with reference to the incident energy J_0, and carrying out the integration, we find the second part I_2 of the light energy reflected upwards to be

$$I_2 = \frac{J_0}{4}\left[\frac{\frac{1}{2}a/\lambda^4}{\frac{1}{2}a/\lambda^4+f(\lambda)}\right]^2$$

In the same way can be obtained the other parts of the total energy I radiated upwards, and we find the sum $I = I_1+I_2+I_3+\ldots$

$$I = \sum_{n=1}^{n=\infty} J_0\left[\tfrac{1}{2}\cdot\frac{\frac{1}{2}a/\lambda^4}{\frac{1}{2}a/\lambda^4+f(\lambda)}\right]^n = J_0\,\frac{\frac{1}{4}a/\lambda^4}{\frac{1}{4}a/\lambda^4+f(\lambda)} \tag{4′}$$

Evidently Eq. (4) allows us to obtain the spectrum of light "reflected" by sea water in all its thickness from the surface to the bottom, if a and $f(\lambda)$ are known. Before passing to the consideration of these quantities however, let us reduce this formula to a somewhat different form.

For simplicity, let us suppose that the sea is illuminated from above by parallel rays falling perpendicularly on its surface. This illumination is composed of two parts, the light of the sun (S_0) and the illumination of the sky (H_0), which over our seas, even the southern ones, is very feebly colored, and therefore we shall not take this coloring into account.[1] Therefore, $I_0=H_0+S_0$. As the light I emitted by the sea, is diffuse, the intensity of interior illumination M_0 will be $M_0=I/\pi$. The final form of Eq. (4′) will therefore be

$$M_0=\frac{H_0+S_0}{\pi}\cdot\frac{\frac{1}{4}(\alpha/\lambda^4)}{\frac{1}{4}(\alpha/\lambda^4)+f(\lambda)} \tag{4}$$

From this we also see that neither the diffusion of rays by the suspended particles, nor their absorption by the water itself (the intrinsic color of the water) should be disregarded. In the first case ($\alpha=0$) we should obtain a perfectly black surface ($M_0=0$), and in the second ($f(\lambda)=0$) a perfectly white one, $M_0=(H_0+S_0)/\pi=$const., independent of λ. The sea would reflect the light in the same way as a white diffusing surface, for which the albedo is one.

2. *The determination of the coefficients of diffusion and absorption.* The absorption of visible rays of light in optically clear water has been studied sufficiently well. In our calculations according to our main formula (4) we have used the numerical values of the coefficient of absorption $f(\lambda)$ found in the above mentioned book of O. v. Aufsess. It appears that this book also contains in a concealed form the data for the determination of the coefficient α. In fact, if we examine the curves that represent the coefficient of absorption in the water of different lakes investigated by Aufsess, as a function of the wave-length, it will be obvious that the characteristic irregularity of these curves shows the composite character of this "coefficient of absorption" which the author ascribes to coloring materials mixed with the water. We have only to subtract from the ordinates of these curves the corresponding ordinates of the curves $f(\lambda)$ (the coefficient of absorption in optically clear water) and the remaining part will come out inversely proportional to the fourth power of the wave-length. The experimental curves of Aufsess appear, then, to express the dependence of the sum of the coefficients of absorption and of diffusion upon the wave-length, i.e. their ordinates are equal to $m=\frac{1}{2}(\alpha/\lambda^4)+f(\lambda)$.

By changing the parameter α, we can get a series of curves for m.

In Fig. 1 are shown 4 curves of this series, curves 1, 2, 3 and 4 corresponding to four different values of α, zero, .004, .020 and .070 respec-

[1] See section 5.

tively. No. 1 shows the coefficient of absorption in optically clear water [$f(\lambda)$]. No. 5, taken from the above mentioned book of Aufsess, was experimentally obtained by him for Staffel Sea.

3. *Calculation of the spectra, neglecting the absorbing effect of suspended particles.* If the function $f(\lambda)$ be known and if the order of magnitude of coefficients α as actually found, is also known, we can calculate a series of typical spectra from formula (4), corresponding to definite values of α. The spectra obtained are represented in Fig. 1, curves 6, 7, and 8 cor-

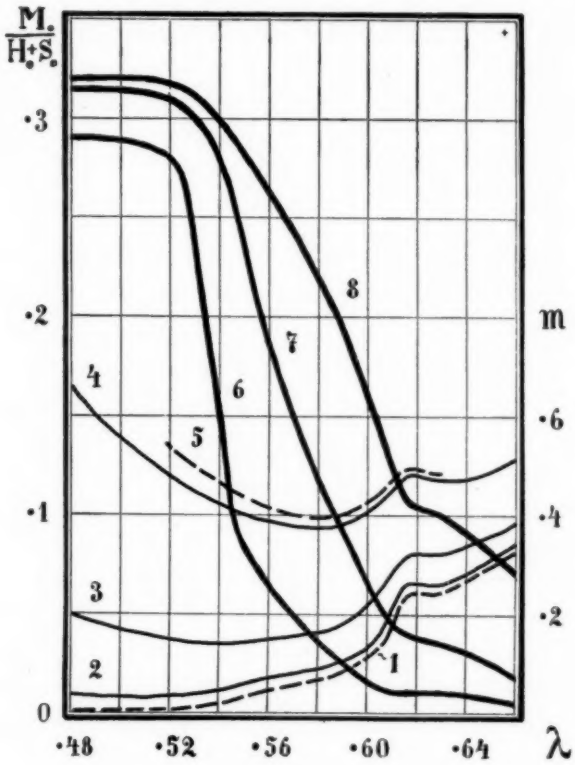

Fig. 1

responding to $\alpha = .004$, .020, and .070, respectively. The figure shows how abruptly the curve 6 falls in the green part of the spectrum and how much absorption there is in the yellow and red. As the coefficient of diffusion becomes larger the curve becomes less steeply inclined and the color of the sea consequently greener and considerably less saturated, i.e. with a large mixture of white.

4. *Influence of suspended particles showing selective reflection.* In deriving Eq. (4), it was supposed that the suspended particles diffused

light without absorbing it. In reality besides such particles (possibly small bubbles of air) the water may contain, especially after a gale, a large amount of finely divided dust or clay particles, plankton, etc., capable of selective reflection and absorption. As these particles are of a comparatively large size, we can, without large error, assume simple reflection and absorption of light by them and restrict the Rayleigh scattering to the smallest suspended particles of which we spoke in §3. When we take into consideration the action of the particles of both kinds and the absorption of light in the water itself, we can obtain results completely analogous to those above.

If the coefficient of reflection of the particle, corresponding to the wavelength λ is $\varphi(\lambda)$, then $\psi(\lambda)=1-\varphi(\lambda)$ will be the corresponding coefficient of absorption. The decrease of light by a stratum of a thickness equal to dz will be

$$dJ=-J\{(1-\beta)\cdot\tfrac{1}{2}(a/\lambda^4)+f(\lambda)+\beta[\varphi(\lambda)+\psi(\lambda)]\}dz$$

where β is the probability of the ray encountering a particle of the second kind, in a path of one meter. Upwards there will be reflected a quantity of energy

$$dI_z=J[(1-\beta)\tfrac{1}{2}a/\lambda^4+\beta\varphi(\lambda)]dz$$

Continuing the analysis in the same way as in section 3 we obtain

$$I=J_0\frac{(1-\beta)\tfrac{1}{4}(a/\lambda^4)+\beta\cdot\tfrac{1}{2}\varphi(\lambda)}{(1-\beta)\tfrac{1}{4}(a/\lambda^4)+f(\lambda)+\beta[1-\tfrac{1}{2}\varphi(\lambda)]} \tag{5'}$$

and finally,

$$M_0=\frac{H_0+S_0}{\pi}\cdot\frac{(1-\beta)\tfrac{1}{4}(a/\lambda^4)+\beta.\tfrac{1}{2}\varphi(\lambda)}{(1-\beta)\tfrac{1}{4}(a/\lambda^4)+f(\lambda)+\beta[1-\tfrac{1}{2}\varphi(\lambda)]} \tag{5}$$

As an example I determined $\varphi(\lambda)$ for brown clay experimentally. From formula (5), which is the most general, were then derived the spectral curves 9, 10 and 11 in Fig. 2. They correspond to different values of β, the concentration of particles of the second kind. The coefficient a is in all cases supposed equal to 0.004 as for the curve 6 of Fig. 1; this curve is also given, for comparison, on Fig. 2.

5. *Influence of the reflected light of the sky.* The diffused light emitted by the sea was investigated in §§3 and 4. This light can be readily observed by looking downward from a steep coast into a deep place or from ship board. But to the observer looking at the sea at an acute angle the coloring of the surface appears always changing, depending greatly upon a number of exterior conditions, chiefly upon the state of the surface, and the form and dimensions of the waves.

Let the ray of vision which comes to the eye from some element of surface, make the angle φ with the perpendicular to this element. Evidently, it is easy to divide it into two component rays I_M and I_H. The first one belongs to the diffused interior light. It reached the element of the surface at some angle ψ with the perpendicular. The second ray

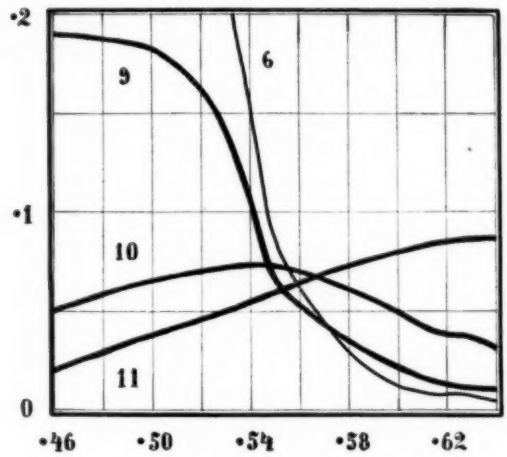

Fig. 2

Curve 9 corresponds to $\beta = 0.02$ (color greenish)
Curve 10 corresponds to $\beta = 0.20$ (color green)
Curve 11 corresponds to $\beta = 1.00$ (color brown).

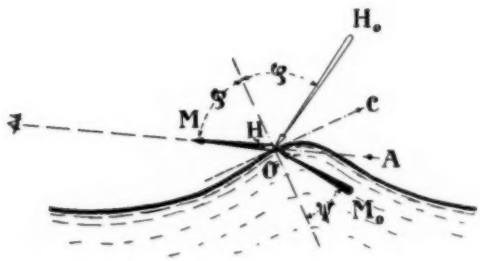

Fig. 3

is the ray of light reflected from the sky, i.e. which has fallen on an element of the surface at the same angle φ with the perpendicular. The intensity of the rays I_M and I_H will depend upon the angle φ according to the well known formulae of Fresnel.

Let us introduce the quantities M and H, the visible brightness of illumination of the surface by the diffused interior light and the reflected light of the sky, respectively, instead of the intensity of the rays I_M and I_H.

Evidently the dependence M upon M_0 and of H upon H_0 will be, by the Fresnel formulae, as follows:

$$M = \tfrac{1}{2}\frac{\sin 2\varphi \cdot \sin 2\psi}{\sin^2(\varphi+\psi)}\left[1+\frac{1}{\cos^2(\varphi-\psi)}\right]\cdot M_0 \tag{6}$$

$$H = \frac{\tfrac{1}{2}\sin^2(\varphi-\psi)}{\sin^2(\varphi+\psi)}\cdot\left[1+\frac{\cos^2(\varphi+\psi)}{\cos^2(\varphi-\psi)}\right]\cdot H_0 \tag{7}$$

Now, taking into account the fact that for water: $\sin\varphi/\sin\psi = 1.32$ it is possible to calculate M and H for different angles φ. Fig. 4 shows curves I, II, III sketched according to Eqs. (6) and (7) in polar coordinates. Curve I represents the brightness of reflected light of the sky, together with the diffused light of the sea; curve II is the brightness of the diffused light of the sea in the blue part of the spectrum (see curve 6 in the Fig. 1); curve III is the brightness of the diffused interior light in the yellow-green part of the spectrum. The relative lengths of the

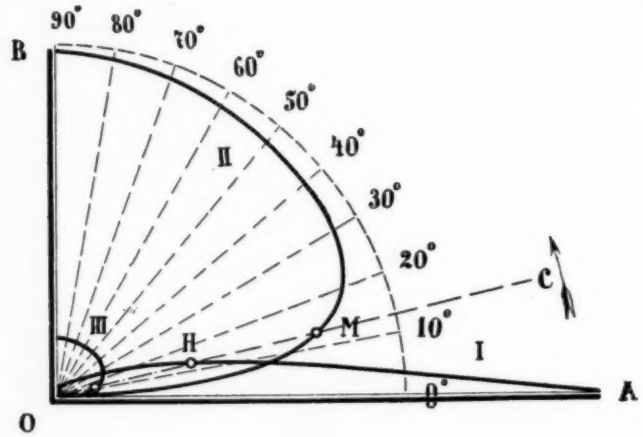

Fig. 4

limited vectors $OA = H_0$ and $OB = M_0$ correspond to the case where $H_0 = S_0$, that case being the usual one according to Bunsen and Roscoe, Pernter and others.

The rays of sight are directed from O towards A. The angle AOC is the angle at which the element of the surface is inclined towards it. From this diagram it is apparent that in calm weather when the surface is horizontal, the angle AOC is most acute and the sea has the same color as the sky (M is nearly zero and H is a maximum). But with comparatively small waves the vector representing H begins to decrease rapidly and the vector M begins to grow, and the sea soon acquires a blue tint. Usually an increase of the intensity of the coloring does not depend

so much upon large waves as upon small secondary ones that run over the large ones.

The sea acquires the deepest blue with so called forced waves that differ greatly from the trochoidal free waves and have a very steep front from the lee side. This difference in color can be very well noticed by any one observing the sea from a ship whose course is perpendicular to the direction of the wind; from the lee side the sea seems much more intensively colored than from the weather side where the surfaces of the waves are more steeply inclined.

6. *Approximate determination of the coefficient of diffusion with the Secchi disk.* The so called Secchi disk is usually employed for measuring the transparency of water. This disk (ordinarily of 30 cm diameter), painted white, red or any other color, is sunk into the sea until it disappears in the surrounding background. The corresponding depth of sinking is taken as a measure of transparency for the corresponding color.

Let us try to define, according to Eq. (4), the correspondence between the depth of disappearance and the coefficient α, upon which it must depend. We must notice that all our results can be applied only to a disk with a small diameter, although, as Secchi showed, a considerable increase of diameter beyond a certain amount does not much increase the depth of sinking, a disk with a diameter of 1.37 metres disappearing at a depth only 15 percent greater than a disk with a diameter one-fifth as great. Having made such a limitation and disregarding the shadow which the disk throws upon the surface of the sea as a result of illumination by the interior light, we will find that the disk disappears at a depth when

$$\frac{(M_0+D_z)-M_0}{M_0}=\frac{D_z}{M_0}=\Delta \tag{8}$$

where D_z is the additional intensity of light which depends upon the depth of sinking of the disk z, and Δ is the least perceptible relative difference in illumination. M_0 is derived from Eq. (4) and D_z can also be obtained with sufficient approximation. In fact, if there were no diffusion, the intensity of light, emitted by the disk at a distance r from it (in a vertical direction), would be:

$$J_r=\mu\frac{J_1\sigma\cos i}{r^2}=\frac{J_1\mu\sigma}{r^2}$$

where J is the intensity of incident light, σ the area of the disk, and μ the albedo. Denoting the compound coefficient of absorption of water $\frac{1}{2}(a/\lambda^4)+f(\lambda)$ by m, we shall find that the decrease of light dJ_r in the distance dz, is

$$dJ_r=-\left[\frac{2J_1\mu\sigma}{r^3}+J_r m\right]dr$$

or $$\left[\frac{2J_1\mu\sigma}{r^3}+mJ_r\right]dr+dJ_r=0$$

The integral of this differential equation between the limits 0 and z is

$$D_z=J=-2J_1\mu\sigma e^{-mz}\int_0^z\frac{e^{mr}}{r^3}dr$$

Or, as $J_1=(H_0+S_0)e^{-mz}$

$$D_z=-2(H_0+S_0)\mu\sigma e^{-2mz}\int_0^z\frac{e^{mr}}{r^3}dr \tag{9}$$

The value of this integral, reduced to a logarithmic integral, can not be found exactly. Applying methods of approximate calculation, and supposing $\Delta=1/133$ (according to Helmholtz) it is not difficult to get the desired relation between the quantity a and the critical depth of sinking of the disk, z. It is obvious that such a calculation would be justified only when the disk as well as the surrounding background emitted monochromatic light. Then calculating the quantities $f(\lambda)$ and a/λ^4 corresponding to this spectral color for every a we could find m and hence, from Eqs. 8, 4, and 3, get z. From this it can be seen, that first of all the blue disk disappears, and last the red one. As, after a great many experiments, it seemed that the white disk disappears at nearly the same depth as the red one, we thought it possible to take $\lambda=0.65\ \mu$ for an approximate calculation, supposing that the white disk disappears nearly at the same depth as the one which could reflect monochromatic rays with $\lambda=0.65$.

Calculations according to Eqs. (8), (4), and (9) furnish the curve in Fig. 5. In the above mentioned book of Aufsess, a curve of the compound coefficient of absorption is shown for Walchensee. Applying this curve we calculate the coefficient a (see §2) to be 0.0142. On our curve a depth of sinking of the Secchi disk of nearly 20 meters corresponds to such a value of a. This is nearly the same as found by Aufsess in the Walchensee, for he observed the disk to disappear at 17 meters in summer and 24 meters in winter. Comparing the value of a given by the curve in Fig. 5 with the depths of disappearance of the disk in different seas,[5] we arrive at the conclusion that of the curves on Fig. 1, No. 6 corresponds to the Black Sea, No. 7 to the Baltic, No. 8 to the White Sea. In the case of the last two seas, there probably exists in them a large quantity of particles of the second kind.

This summer I hope to make an experimental examination of this theory, using specially constructed instruments. However I have al-

[5] J. Shokalsky, Oceanography., Petrograd, 1917.

ready been able to complete several controlling laboratory experiments and calculations.

7. *Synthesis of colors. Perceptible color of diffused radiation.* It appeared possible to effect such a synthesis experimentally with the aid of a very simple method, which may prove to be useful in other cases where it is desired to synthesize colors according to a given spectral curve.

The spectrum of white light, obtained in the camera of a precisely graduated spectograph was converged by a lens and directed on a screen where it formed a white image. Into the camera (at the place where the

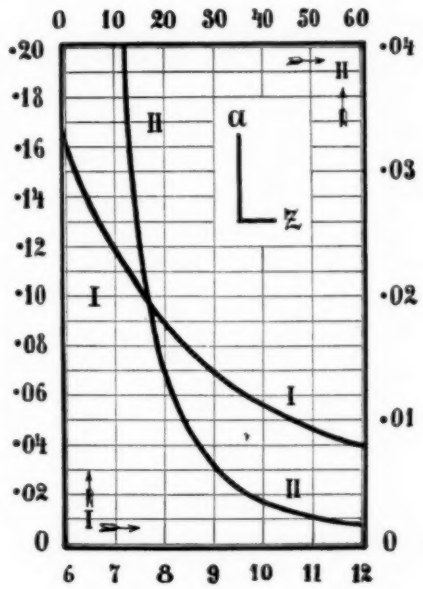

Fig. 5

real image of the spectrum was obtained) a partition was set, in which a slit precisely fitting one of the calculated curves Nos. 6, 7, 8, 9, 10 and 11 was made. The scale of the abscissae was of course different in different parts of the spectrum. Due to such a slit the relative brightness in any part of the spectrum, depending on the breadth of the slit in the corresponding place, was made proportional to the corresponding ordinate of the theoretically obtained curve. By observing the alteration of colors upon the screen beyond the converging lens, it was easy to ascertain that the colors obtained corresponded closely to the actual ones. For the purpose of demonstrating the synthesis of colors, this experiment was somewhat altered. Upon a rotating glass cylinder was placed a gelatin

film on which a spectrum occupying half the circumference of the cylinder, the other half remaining transparent, was painted with transparent colors. The spectrum was covered with an opaque template in which a slit corresponding to one or other spectral curve was cut out. The cylinder was placed between the condenser and the object glass of a projection lantern, the focus of the condensor lying on the axis of rotation of the cylinder which was perpendicular to the optical axis of the lantern. Such a construction easily allowed a synthesis of colors; for the intensity of light in each part of the spectrum was proportional to the corresponding ordinate of the theoretical curve (Nos. 6-11).

Results fully concordant with the described experiment can also be obtained by means of a synthesis of colors, based upon the ion theory of color vision of P. P. Lasareff.[6] In accordance with this theory, there were sketched, in each part of the spectrum, three curves characterising the quantity of pigments sensitive to 1) red, 2) green and 3) violet, which are decomposed in the eye by the influence of white light. Multiplying the ordinates of these three curves by the corresponding ordinates of our spectral curve (Nos. 6, 7, 8) there are drawn three new curves for each spectral curve, showing the quantity of all the three pigments affected in the eye by colored light. By evaluating the relative areas of these curves, we obtain the resultant color perceived and its saturation value. The results of synthesis for four of the most typical spectral curves, are given in the following table.

TABLE I

No. of Curve	α	β	Particles of 1st kind	Particles of 2nd kind	By theory of P. P. Lasareff		Color obtained by direct synthesis
					λ percept.	Saturation	
6	0.004	0	Few	None	0.48μ	3.0	Blue, saturated
7	0.020	0	Many	None	0.50μ	1.5	Greenish-blue (pale)
10	0.004	0.2	Few	Few	0.55μ	0.45	Green
11	0.004	1.0	Few	Many	0.61μ	0.39	Brown (pale)

It is clear that the whole scale of colors from saturated blue to light brown is easily explained without introducing the hypothesis of colors added to the water, as did v. Aufsess.

Here it has been supposed that there are suspended in the water, particles of clay; of course particles of other origin, plankton, etc., can produce, according to formula (5), a great variety of colors.

[6] P. P. Lasareff. Bulletin de l'Académie des Sciences de Russie, p. 1051, 1918, Petrograd, and Isvestija Fizicheskago Instituta I, 113, 1920, Moscow.

8. *Photometry of artificial turbid media in reflected light.* As Fig. 1 shows, the total coefficient of absorption and diffusion for natural water is a quantity of the order 0.1—1.0, if it is applied to a wave-length 1μ and a stratum of water 1 meter thick. It is evident that laboratory experiments with photometry in reflected light cannot be made with such liquids and it is therefore necessary to use some liquid more intensively colored than water, and in which the particles are suspended in a greater concentration. It was very tedious choosing colors and suspensions, as conditions had to be created to prevent suspended particles from being themselves colored and a number of other undesirable phenomena had to be avoided. After a number of tests it was found that an acceptable color, because of its curve of absorption and resemblance to water, is Rodulin blue and the most suitable suspension is the colloidal solution of rosin in alcohol, drops of which were added to water colored by Rodulin. With the aid of a König-Martens spectra-photometer (1) the coefficient of absorption for Rodulin-colored water and (2) the total coefficient of absorption and diffusion for the same liquid

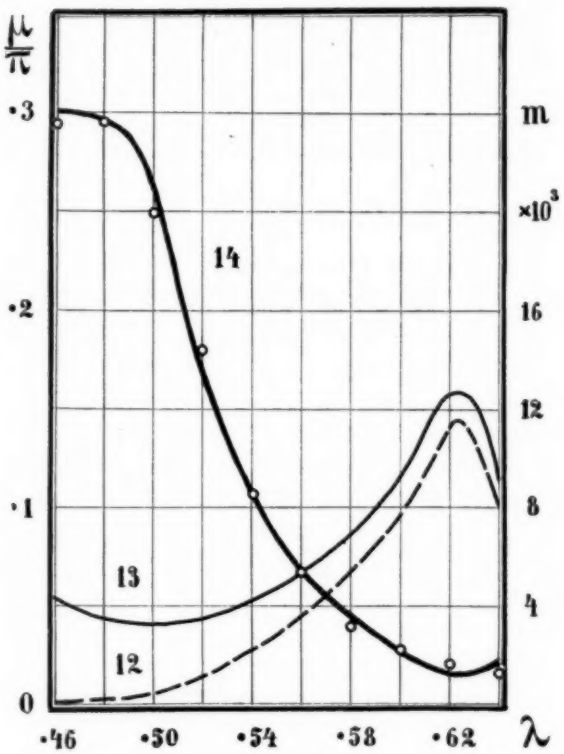

Fig. 6

with an admixture of suspended particles were determined and also for verification, (3) coefficients of diffusion for clean water in which the same quantity of suspension was added as in case (2). These results made possible a calculation of the spectrum of light reflected by our "model of the sea" according to formula (4).

In Fig. 6, curves (12) and (13) accordingly represent the coefficients (1) of absorption for Rodulin solution and (2) of absorption and diffusion for the same solution with suspended particles of rosin (the coefficients relate to a wave length of 1μ and to a layer thickness of 1cm); curve (14) represents the spectrum of reflected light for my "model of the sea," calculated according to our formula (4), that is the ratio of the intensity of the reflected spectral ray to that of the corresponding incident ray, or the coefficient of reflection of the sea divided by π. Then,

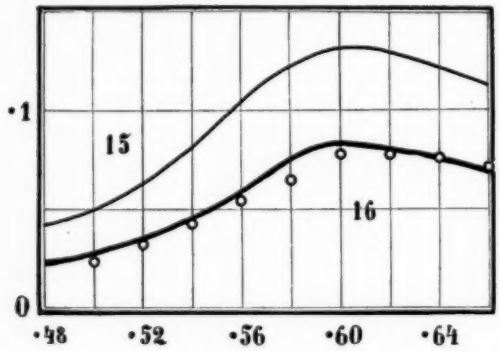

Fig. 7

with the aid of a spectrophotometer, the light reflected by the model of the sea, was compared with the incident light and the experimental points obtained were marked on Fig. 6. It is easy to ascertain that they fully coincide with the curve 3, calculated theoretically.

To verify the formula (5), which takes into account the effect of particles of the second kind, a similar experiment was made in clean water to which there was added a certain quantity of ochre, which produces large-grained particles that do not sink very rapidly. In the first place, with the aid of photometry, the coefficient of reflection, $\varphi(\lambda)$, for dry ochre was obtained, and then it was possible to calculate the spectrum of reflected light according to formula (5), which here takes the simpler form,

$$M_0 = \frac{H_0 + S_0}{\pi} \cdot \frac{\frac{1}{2}\varphi(\lambda)}{1 - \frac{1}{2}\varphi(\lambda)}$$

or:

$$\frac{\mu}{\pi} = \frac{\frac{1}{2}\varphi(\lambda)}{1 - \frac{1}{2}\varphi(\lambda)},$$ because $a = 0$ and $f(\lambda) = 0$, where

μ is "the coefficient of reflection" of our yellow "sea." Both curves $\varphi(\lambda)$ and μ are drawn in Fig. 7, where they are denoted by Nos. 15 and 16.

Experimental points on the same diagram were obtained by direct photometry in reflected light. They lie sufficiently close to the calculated spectral curve (16) although they do not coincide with it as well as in Fig. 6.

9. *On the applicability of the theoretical considerations of §7 to observation with the Secchi disk.* The experimental material collected by O.v. Aufsess, proves just the opposite of his conclusions with regard to the causes of color of lakes and wholly supports my assumptions in deriving formula (4). It is sufficient to look over the last column of Table II which contains the results for Arbersee, calculated by me in accordance with Aufsess's dissertation, to be convinced of the existence of Lord Rayleigh's effect.

TABLE II

λ :	0.52	0.54	0.56	0.58	0.60	0.62	0.64
$m-f(\lambda)$:	1.0	0.86	0.72	0.65	0.56	0.50	0.45
$[m-f(\lambda)]\lambda^4$:	0.0731	0.0731	0.0708	0.0735	0.0726	0.0739	0.0755

It is obvious that the product of the fourth power of the wave-length by the difference between the coefficient of absorption for lake water and for clean water remains constant and near to the mean value 0.0732. So the water of the lake can be looked upon as Rayleigh's turbid medium. The value of the coefficient of diffusion for Arbersee will, obviously, be $a=2\times 0.0732=0.146$.

By extrapolating the curve in Fig. 5, it is easy to calculate the depth of sinking of the Secchi disk in this lake; the depth appears to be equal to $z=6.3$ meters; Aufsess' experiments showed that in reality in the Arbersee the Secchi disk disappears at a depth of 6 meters, which agrees with our calculated quantity.

By calculating tables analogous to that of II, for other lakes for which the observations by Aufsess gave a gradual change of coefficient of absorption with the change of wave-length, it can be demonstrated that for them also our conclusions are justified. For Staffelsee, calculations gave $z=8.5$ meters, and the real depth at which the Secchi disk disappeared was 7.5; for Kochelssee calculations gave 14.7 meters and observations by Aufsess 16(?) meters; for Walchensee our calculations gave $z=19.6$ meters and observations by Aufsess 20.2. Taking in account the roughness of observations with the Secchi disk and the approximations introduced into the calculations, this agreement between theoretical and experimental results can be considered satisfactory.

Conclusions

1. The coloring of the sea depends on four factors: (a) Selective absorption of light by water; (b) diffusion of light by tiny suspended particles (probably small bubbles of air, or of other gas contained in it; (c) selective reflections of light by particles of the second order (particles of fine dust, plankton etc.); (d) admixture of the reflected light of the sky.

2. In the present work the spectrum of the diffused light emitted by the sea is calculated for typical cases.

3. The relation is found between the inclination of waves running over the surface of the sea, and the intensity of its color.

4. A method is given by which an approximate calculation can be made of the coefficient of diffusion, with the aid of an ordinary Secchi disk.

5. Fig. 4 allows us to explain the intense color of mountain lakes where the surrounding mountains cover part of the sky near the horizon. The zones of the sky are reflected in water only at a considerable angle. The admixture of white color is therefore not great and the observer sees the color of the lake only as it is colored by the diffused interior light.

In conclusion, I desire to express my thanks to Prof. P. P. Lasareff, Fellow of the Academy of Sciences of Russia, for advice in questions of physiological optics.

Physics Department of the Scientific Institution,
Moscow
December 1922.